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CONTENTS

The Textile Research Conference 107

The Research on Wool Fiber Damage 109

Report of Committee Chairman R. A. Lukens 111

Tentative Program for Study of Wool Fiber Damage 114

Combination of Silk Fibroin with Acid and with Base. Leland F. Gleysteen and Milton Harris. *A Textile Foundation Publication* 117

Fundamental Properties of Textile Wastes. IX. Concentration of Sulfur Black Dyes by Froth Flotation. L. C. Surprenant, J. E. Magoffin, and F. K. Cameron. *A Textile Foundation Publication* 126

Factors Influencing Flocculation and Precipitation. Influence of Initial Particle Size. Ellington M. Beavers, James E. Magoffin, and Frank K. Cameron. *A Textile Foundation Publication* 139

The Variation of Raw Cotton Constituents with Physical Properties. R. F. Nickerson, T. D. Fontaine, and C. B. Leape 154

Terms Relating to Hand of Fabrics 158

Abstracts 159

Advertisement: Henry L. Scott Co., Providence, R. I. 106

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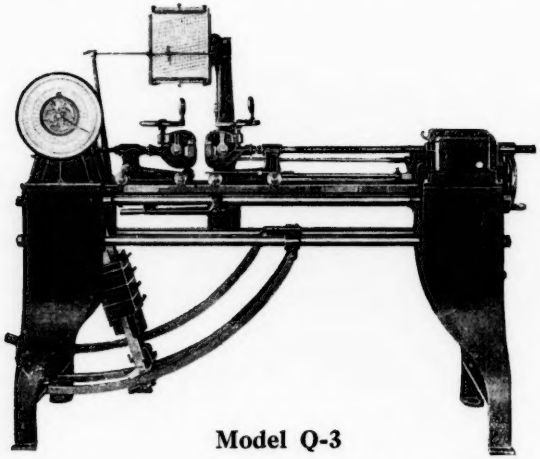

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TEXTILE RESEARCH

Publication of

United States Institute for Textile Research, Inc.
and for the Released Research Reports of
The Textile Foundation, Inc.

The Textile Research Conference

THE Research Conference that was held in conjunction with the annual meeting of the Institute at the Hotel Pennsylvania, New York City, Nov. 14, was aptly described by the presiding officer, Chairman W. D. Appel of the Research Council, as a roundup of four Institute researches in progress or planned that are concerned with rather widely diverse lines and that represent work in four different stages. These, he stated, illustrate how the Institute is prepared to cooperate with other agencies, and to organize independently financed research projects. These projects were described by the chairmen of their respective Administrative Committees, and are as follows:

(1) *The Warp Sizing of Spun Rayon.* Carl R. Harris, Chairman. Wholly financed through the Institute, and in progress since Oct. 1 at North Carolina State College Textile School, Raleigh, N. C.

(2) *Textile Drying.* Dr. A. C. Walker, Chairman. Wholly financed through the Institute, and recently completed after having been conducted for three years at the National Bureau of Standards. Plans for its continuance are being considered.

(3) *Inventory Policies and Statistical Guides.* Fessenden S. Blanchard, Chairman. An economic research suggested and organized by the Institute's Committee on Economic Research. Wholly financed by The Textile Foundation, and now approaching completion after having been conducted for two years at the Wharton School of Finance and Commerce, University of Pennsylvania.

(4) *Wool Fiber Damage in Processing.* Rinaldo A. Lukens, Chairman. A new project to be wholly financed through the Institute. The subject of discussion at a research conference a year ago, and since then authorized as a research project by the Institute Board of Directors. Financing of the research is now in progress. The National Bureau of Standards has been selected as the place for the study.

Status of Researches

Chairman Harris of the Administrative Committee for the warp sizing research reported that F. Gordon Cobb, who is in direct charge of the work, and his associate, Mr. Biggers, a recent graduate of North Carolina State College, have been engaged thus far in planning and preparing the mechanics of the study so that small warps, instead of full sized ones, may be used in the preliminary experimental tests. For instance, they have developed an ingenious device for running abrasion tests that will closely approximate the abrasive and stress-strain action of the loom on the sized warps. He regretted that so few of the cooperators had filled out and re-

turned the questionnaires mailed to them, and had thus failed to indicate their preference of the basic type of fabric for use in experimental work. Lacking this information the committee will make the selection and proceed with the work.

Chairman Blanchard of the Committee on Economic Research reported that the study of Inventory Policies and Statistical Guides has been completed, is now being written up, and should be ready for publication in book form early in the new year.

Utilization of Research Results by Industry

Chairman Walker of the Administrative Committee for the Textile Drying Research reviewed the results of the three-year study only briefly, noting that the papers describing the work of the first two years had been published in *Textile Research;* that those covering work of the third year are still going to cooperators, and eventually will be released for publication. He stated that some of the results had been accepted as so new and valuable as to warrant incorporation in standard reference works. He expressed himself as confident that some of the results, when studied by research men and engineers having some knowledge of the needs of the textile industry, should solve some problems of commercial value to the industry. "However," he said, "you have to have men of imagination and ingenuity in the development organization, and also in the manufacturing branch, in order to make use of the experimental things we get." He did not believe it to be the function of a research organization like the Institute to be able to go into a mill and say "Here, you can save money this way."

Dr. Walker clarified and emphasized the preceding statements by describing the manner in which the results of a purely academic piece of research of the Bell Telephone Laboratories, with which he is associated, were first ingeniously interpreted and finally applied in a commercially profitable manner. The research involved the question of why silk, which takes up more moisture than cotton at any given humidity condition, had the better electrical properties. It happened to be true in this case that the responsible research men visualized possible commercial application of the results of the study, for they had found that the washing in water of both silk and cotton greatly increased their electrical properties—in the case of cotton as much as one hundred fold. However, it was not until they had interested the telephone company's developmental engineers in the possible commercial value of the discoveries, and they in turn had carried developmental work far enough to prove interesting to the manufacturing technicians, that the two latter groups got together and cooperated in applying the findings practically and upon a commercially profitable basis—cotton yarn displacing the relatively expensive silk for many electrical insulating purposes. It can be plainly inferred from this story that if more textile organizations had capable engineers and technical men who could and would have as one of their important duties the study of textile research results, more of the latter would be developed and commercially applied. When that happens the textile research organizations will have been helped over their most difficult hurdle—the sale of research to the industry.

That there are individual concerns that are already capitalizing textile research results was demonstrated at this conference by the following statement:

"I would like to add a word of thanks and appreciation for the fine work which Mr. Wiegerink did under the direction of Dr. Walker. . . . I know that in our own business we have had results which have paid us many times for the money that we put up for the textile drying research. I can safely say that every month we get back the money we put into it. I don't know exactly what the textile drying research cost, but I know that it was in the neighborhood of $12,000 or $13,000. I know that that amount is just simply infinitesimal compared with the splendid results which were obtained, and I think that we all owe a debt of gratitude to Dr. Walker."—Mr. Alban Eavenson, Eavenson & Levering Co., Camden, N. J.

The Research on Wool Fiber Damage

Because it involved a new research project whose program had been approved by the Institute's Directors, and was ready for cooperative financing, the report of the Administrative Committee for the study of Wool Fiber Damage in Processing, as presented by Chairman Rinaldo A. Lukens, and the discussion which followed, were the major features of the conference. Chairman Lukens' report and the research program are published in this issue.

Although the report had the approval of the whole committee, one of its members, Hugh Christison, stated during the discussion period that he would have preferred a more direct approach to the study of wool damage and its causes. His statement was in part as follows: "I think that if the committee would go at the wool damage question from the point of view of trying to develop adequate methods for accurately determining causes of damage by light, heat, bacteria, etc., they would be doing the industry a greater service than by using resiliency tests for evaluating fiber damage. There is no question but that resiliency is important. I think that if the study as planned is carried to a conclusion it will tell manufacturers a lot of things about how to handle their goods so as to obtain better finishes. I still maintain that to do the industry the most good and to give it the most for its money, would be to develop adequate tests for detection of fiber damage and for determining its causes."

Resiliency as a Measure of Wool Damage

Dr. Milton Harris, a member of the Administrative Committee and director of research for the Textile Foundation at the National Bureau of Standards, was credited by Chairman Lukens with the development and proposed use of the resiliency test method, and was asked to explain it. This he did extemporaneously and in part as follows: All textile fibers have different physical structures, and we are interested in each of them for their special features. If we were interested only in strength we probably would not be interested in wool fibers, because wool fibers are probably the weakest of all our important fibers. Wool fibers run from some 15,000 to 30,000 pounds per square inch in tensile strength, whereas nylon, silk and cotton will run anywhere from about 70,000 to 120,000 pounds per square inch. The rayons will vary in between, depending upon how they are prepared. So you see that wool would have a lot of trouble competing

with many other fibers on the basis of strength. If you will look at the types of fabrics into which wool fibers go, and will find out why they are used in those fabrics, you will really have to come to the conclusion that wool fibers are used because of their high degree of resiliency.

Resiliency may or may not be important to the wool trade. I, personally, feel that it is. I feel that the wool manufacturer who disregards resiliency would be pretty much in the position of the man who gave his impression of the scenery in Switzerland when he said "If you take away the mountains, what have you got?" You can take a wool fiber and stretch it 10%, and it will come back to its original position. You can stretch it 20, 30, and even 40% in the wet state and it will still come back to its original position. Under certain conditions you can stretch it almost 100%, at the same time subjecting it to quite rapid loading.

We have all been brought up to think of silk, and more recently of nylon, as highly resilient fibers compared with wool. Silk offers only a short-range resiliency. If you stretch a wet silk fiber 8% of its original length, it will immediately recover only about half of the elongation, and if you will stretch it 10% it will recover only about 40%. Nylon appears to behave similarly. The rayons and cottons have even lower degrees of resiliency. I think that this presents a good example of what the wool man has. He has a head start of perhaps 20 or 30% on what I would call long range resiliency, and I think that this is the difference between wool being used, or not being used, as a textile fiber.

Concerning the single fiber method of testing that Mr. Lukens has asked me to explain, I will speak briefly. I think that you have all had the experience of treating wool yarn by methods that you are positive would damage a wool fiber, and yet, on determining tensile strengths, you actually get an increase in yarn strength. There are planty of chemical reagents that are sold with the claim that they will increase yarn strength, but which can be shown to damage the fiber very badly, especially its wearing quality, as well as many of its other good characteristics. I have seen reagents which can destroy much of the resiliency of the wool fiber without an appreciable decrease in its tensile strength. Therefore I think that the usual tensile strength measurements, while they serve some useful purpose, can be carried too far, and one can get very anomalous results by relying upon them to too great an extent.

On the other hand, it is a remarkable fact (and it sounds a bit unbelievable) that if you take a single wool fiber and run a stress-strain curve of it (that is, stretch it up to 30% and allow it to come back) it will return in less than a minute to within a fraction of a percent of its original length. If you stretch that fiber again (after allowing time for relaxation) it will follow, about as closely as you can measure, the same path that it followed before. You can then take that fiber and treat it by any chemical process that you care to, scour it, or carbonize it, and you can, by again running a stress-strain curve, accurately measure the decrease in the strength of that fiber, and also its resiliency; that is, the ability to come back to its original position. Therefore one has a very sensitive measure of fiber degradation both from the standpoint of strength and the far more important characteristic, resiliency. While this working with a single fiber may sound tedious, one can, by doing a few experiments on three or four fibers, get more information than by running many yarn tests.

Report of Committee Chairman R. A. Lukens

THE need for a study of wool manufacturing processes from the standpoint of the effects upon the properties of the fiber, was recommended to the Institute informally about three years ago, and at the annual meeting held in New York on November 2nd of last year an open conference was held on the subject of "Wool Fiber Damage in Processing."

Prior to the open discussion, several papers were presented covering new knowledge of the chemical properties, and the physics and microscopic structure of wool, and stressing the importance of a better understanding of the causes of fiber degradation on the part of the wool manufacturer.

No manufacturer enjoys being told that his methods of processing are seriously damaging his raw material, yet a representative group of woolen and worsted men who participated in the open conference not only made no effort to refute this reflection upon their technical skill, but reasserted its correctness, and expressed the hope that something might be accomplished toward reducing or eliminating this type of wool fiber damage by additional chemical and physical research, properly directd and conducted.

It was recognized also that any reduction in the amount of fiber damage, which is now accepted as an unavoidable result of the manufacturing process, will not only result in the production of higher quality and better wearing products, but that substantial savings in manufacturing costs will automatically follow, through lessened need of costly reprocessing and a smaller percentage of waste and spoilage.

The Committee, which was subsequently appointed by the Research Council to formulate a workable program of research that would offer sufficient promise of practical results to warrant the approval of the Institute and the financial support of the industry, has been working on the problem for the past year.

It was obviously impractical to tackle the job of making a separte intensive study of each one of the many processes which occur in woolen and worsted manufacturing, from raw material to finished fabric, in an effort to improve upon or perfect the technique of each one. The Committee was convinced, however, that the development of more exact knowledge of the behavior of the wool fiber, when subjected to the various chemical and physical treatments characteristic of the manufacturing processes, would make it possible to establish tolerances, or safe working ranges, for the information and guidance of the manufacturer. Furthermore, this line of investigation would not only shed light on the effect of single processes on the fiber, but would also permit an observation of the cumulative effects of the various processes which are included in the manufacturing cycle. This is not possible with the testing methods now available, as those designed to measure breaking strength, or elongation at the break, are influenced by the construction of yarn or cloth, and most of the chemical test methods measure only very specific changes in the fiber, and for the most part offer few clues to the ultimate effect upon its physical characterisites.

The Committee has been urged to build its program around the objective of developing a method, or methods, for determining the causes of damage in finished cloth. It is the opinion of the majority of the Committee members, however, that this would definitely limit the research to an effort to improve upon testing methods which have been developed over

a long period of time by many scientific investigators in this field. When confronted with the accomplished fact of damaged cloth, whether it be physical damage, finishing or dyeing faults, there is no one test which will point unerringly to the cause, nor can such a single test be developed. The decision as to what tests are indicated is based upon judgment and experience, and a knowledge of reactions which may occur when there is a departure from the prescribed routine of processing.

It is the purpose of the type of research recommended by the Committee to test the existing theories concerning the reaction of the wool fiber to given treatments and conditions, and to determine the working procedure under which a minimum amount of fiber damage will result. Such tested knowledge of fiber behavior will simplify the decision to be made when confronted with the necessity of verifying the diagnosis of cause of damage in the finshed fabric, and offers not only some prospect of definite assistance in a reasonable period of time but, what is even more important, can be the means of preventing these damages before they occur.

In considering the study of individual wool fibers as a medium for the development of basic knowledge that could be of practical value in improving upon processing methods, the Committee realizes it is making a radical departure from the orthodox methods heretofore used of observing the fiber reactions en masse, from the raw material state through yarn and cloth, and such an approach is only possible because of the recent development of new test methods and advances in knowledge of the chemistry and physics of the fiber.

Two fundamental problems are presented: First, there must be some one characteristic of the wool fiber, having a direct relationship to its utility, that could be singled out for study under controlled test conditions, and used as a common denominator for evaluating changes observed in processing. Secondly, a sufficiently sensitive method for estimating changes in this particular property of the fiber must be available.

The one property which distinguishes the physical behavior of wool from the other important commercial textile fibers is resiliency. If silk and nylon are considered to have a good degree of resiliency, cotton poor resiliency, and the various rayons in more or less intermediate positions, then wool must be considered to have an extremely high degree of resiliency. It is unquestionably this high degree of resiliency which has made wool the most valued fiber for a wide variety of textile materials, such as clothing, blankets, carpets, etc. In such fabrics, resiliency plays an all-important part. For example, the pile of the carpet must be able to return to a more or less erect position after it has been deformed; the warmth of a blanket depends to a great extent on the ability of the fiber to maintain a porous structure throughout the fabric; the warmth of clothing materials, such as used in dresses, suits and overcoats, depends on resiliency for the same reason, and in addition this property of the wool fiber allows such clothing material to retain its general shape, hold its press, and quickly recover from a crushed or wrinkled condition.

This important relationship of wool to other fibers is one which woolen manufacturers generally have failed to recognize and emphasize. Since it follows that wool will be an important commercial textile so long as this difference is maintained, it is all important for the manufacturer to retain as much of the original resiliency of the natural fiber as possible, or even attempt to increase it.

It is a well known fact that varying proportions of the resiliency may be destroyed during the numerous processes to which wool is subjected during manufacturing. This generally manifests itself in the form of a so-called "dead" fabric. There are numerous chemical treatments which badly degrade wool fibers to produce a profound lowering of resiliency, but which actually increase the apparent tensile strength of yarns, as they are commonly measured. It should be remembered, however, that the wool fiber does not owe its preferred position among textile fibers to its strength, being inferior to cotton and many synthetics in this respect. Its ability to felt and impart a distinctive life or hand to a finished fabric earns it a position apart from other fibers, which position will be endangered unless its natural resilient properties are unimpaired in the manufacturing processes.

So far as the Committee has been able to ascertain, no information is available at present pertaining to the effect of the various processes of wool manufacture on resiliency. The chief obstacle heretofore in making such an investigation has been the lack of a reliable test method. During the course of the Textile Foundation researches it was necessary to develop such a method in order to evaluate a number of the changes which were being attempted in the physical characteristics of the wool fiber. This method has proved to be so successful that it is now recommended as applicable to the carrying out of the program of research which the Committee is proposing, based upon the effect of processing upon the resiliency of the wool fiber. It should be clearly understood that the use of this testing technique, in its present form, is not suggested for individual textile mills, but only as a research tool for setting up tolerances that could be recommended to wool manufacturers.

Briefly, this method involves the study of the resilient characteristic of a single wool fiber. While at first thought this procedure may appear tedious, it must be pointed out that many fibers can be studied in a day, and that the information obtained from such studies is very accurate and readily interpretable. When an individual wool fiber is gradually loaded under suitable conditions until it elongates 30%, and is then gradually unloaded, and the elongation plotted as a function of the load, a curve is obtained which is highly characteristic of the particular fiber; it is reproduced if the test is repeated, and is very sensitive to changes in the fiber. In the fundamental work on the wool fiber carried on by the Research Associateship of the Textile Foundation, under the direction of Dr. Milton Harris, all changes in the chemical or physical structure of the fiber have manifested themselves in the resiliency measurements obtained by this testing method.

As outlined in detail in the tentative program which is submitted herewith by the Committee, fibers are to be made the basis for the study, as the properties of yarn and fabrics depend upon fiber properties, but yarns and fabrics will also be tested for check purposes.

In addition to establishing tolerances for exposure to acids, alkalis, bleaching agents, detergents, soaps, oils, sizing, steam, temperature, humidity, moisture, light, bacteria, etc., work is planned on the problem of dye absorption, and microscopic observations will be made throughout the experiments. Abrasion tests will be made on yarns by a method in which yarn abrades yarn.

A number of special problems and tests which have been referred to the Committee for consideration will be included in the research. These include the development of a test for grading felting ability of wool, the relation of drying to previous processing, and means for determining the causes of damage from an examination of the damaged wool.

The fact that considerable fundamental work on the wool fiber has already been done by the Textile Foundation, the results of which, together with the fiber testing method previously described, are available to whatever facility may be established for the carrying out of this proposed research on wool damage, is a fortunate circumstance, and should make possible some tangible results during the first year. Most of the required literature for review at the start of the project is readily available, and with the facilities which can be arranged for at the Bureau of Standards in Washington, the work can be promptly initiated and carried on effectively at a nominal cost.

The information that can be developed from this research program is of a type not now obtainable at any price, and should be of incalculable value not only to the manufacturers of materials of wool but also to the raw material branch of the industry which is vitally interested in preserving a market for wool and its products. Such a program should enlist the financial support of a large section of the wool industry, but, if need be, can be carried through the first year by a very modest outlay on the part of a small group of 25 to 50 cooperators, who are willing to gamble a small stake on the prospect of a large return.

Tentative Program for Study of Wool Fiber Damage

A SURVEY of wool manufacturing processes from the greasy raw wool to the finished fabric will be made with respect to the changes, both desirable and undesirable, which the fiber undergoes in each stage of typical processing and the cumulative effects of such changes. This survey is made possible by new test methods, and desirable by advances in our knowledge of the chemistry and physics of the fiber. The results should point the way to economies in the methods of processing wool and make possible improvements in the quality of wool products.

The study will be conducted along two parallel lines. In the first line of work, samples of wool will be taken at each stage of typical commercial processing in cooperating mills, both woolen and worsted, and changes in the properties will be determined. The elastic properties of individual fibers, the resiliency of fiber masss, dye absorption, ability to felt, and resistance to abrasion will receive special attention.

In the second line of work, individual wool fibers will be "calibrated" with respect to certain stress-strain characteristics, then subjected to the same conditions as the commercially processed fibers, insofar as this is feasible, and again tested to detect changes in the physical properties. Calibrated fibers will be subjected to conditions characteristic of each process as well as to the succession of conditions wool has been subjected to when it arrives at each stage of processing.

The results of the two lines of work will be correlated in an attempt to obtain a direct relation between mill practice and laboratory testing.

Explanatory Notes

(1) *Cumulative effects are considered important.* There have been many studies of the effects of various processing conditions on wool. The present study will depart from them in emphasizing the cumulative effects and the relationhips of a process to the effects of earlier processing. Mechanical processing, including carding, combing, drawing, and spinning, will receive the same consideration as wet and chemical processing, like scouring, carbonizing, dyeing and fulling.

(2) *Fibers to be made the basis for the study.* Changes in the fibers are basic. The properties of yarns and fabrics depend upon the fiber properties. Very sensitive methods for measuring fiber properties are available. Accordingly, testing of individual fiber properties will be stressed, though yarns and fabrics will also be tested.

(3) *Properties to be studied include:*

(a) *Elastic properties of individual fibers.* When an individual wool fiber is gradually loaded under suitable conditions until it elongates 30 per cent and then is gradually unloaded and the elongation plotted as a function of the load, a curve is obtained which is highly characteristic of the particular fiber, is reproduced if the test is repeated, and is very sensitive to changes in the fiber. The work on individual fibers will be centered around this test, which has proved to be of great value in the work of the Textile Foundation on wool.

(b) *Resilience of wool.* The resilience of fiber masses and of the wool in the form of yarns and fabrics will be measured. This is one of the most important properties to be studied since it is directly related to the "liveliness," "loftiness," or "hand" of wool and its products. It may be possible to correlate results of this test with the tests of elastic properties of individual fibers.

(c) *Ability of wool to felt.* Since the value of wool for many uses depends upon its ability to felt, any changes in the property resulting from processing will be observed. The development of a method for testing and grading felting ability will be undertaken.

(d) *Resistance to abrasion.* A yarn abrasion test in which yarn abrades yarn will be used. The yarns will be subjected to the various processes just as the fibers will be in the second line of attack.

(e) *Dye absorption.* The effects of processing on the color of the processed wool when it is dyed with typical dyes and with dyes which are particularly sensitive to changes in the wool will be determined. Defects in wool products often become noticeable through uneven dyeing. The dyeing studies may lead to means for correlating observed damage with its cause.

(f) *Microscopic changes.* Changes in the appearance and structure of the fiber that can be observed with the aid of a microscope will be noted and photomicrographic records will be made.

(4) *Tolerances for exposure to the agencies listed below will be tabulated* for the information of the subscribers on the basis of results available in the literature, experience during the survey, and, where necessary, laboratory experiments:

Acids	Soaps	Temperature
Alkalis	Oils	Humidity
Bleaching agents	Steam	Moisture
Detergents	Sizing	Light

(5) *Special problems to be considered.* A number of special problems and tests in which prospective subscribers have expressed an interest will receive consideration. They include:

(a) Development of a test for grading felting ability.
(b) Relation of drying to previous processing.
(c) Means for determining causes of damage from an examination of the damaged wool.

(6) *The processes to be studied include:* Scouring, bleaching, carbonizing, drying, dyeing, picking, carding, spinning, fulling, finishing, wet and dry, steaming and decating, pressing, abrasion. In addition, the effects of bacterial damage at various stages of processing and on subsequent processing will be noted.

Administration Committee

Rinaldo A. Lukens, Chairman

Hugh Christison
Dr. Milton Harris
E. D. Walen
Dr. A. C. Walker
Dr. Werner von Bergen

Combination of Silk Fibroin with Acid and with Base

By LELAND F. GLEYSTEEN and MILTON HARRIS *

A Textile Foundation Publication

Abstract

Silk contains a number of acidic and basic groups. The state of combination and the behavior of these groups are important in influencing the tensile and elastic properties of the fibroin and the adsorption of moisture and dyes.

As part of a broad research program of the Textile Foundation Research Associateship at the National Bureau of Standards on the acidic and basic properties of fibers, this investigation was undertaken to determine the relationship between the quantities of hydrochloric acid and potassium hydroxide taken up by fibroin from solutions and the concentrations of those solutions. The effect of added potassium chloride was also studied. In general, it has been possible to correlate the several parts of the titration curves of proteins with their amino acid contents, but our knowledge of the rôle of the phenolic hydroxyl groups of tyrosine has always been uncertain. Silk fibroin, however, contains such a large proportion of tyrosine as to assure practically an indication of the rôle of the phenolic hydroxyl groups of tyrosine simply by the magnitude of the base-binding capacity. In order to investigate more carefully the part taken by these groups, a titration curve was obtained for methylated fibroin in which most of the hydroxyl groups had been converted into nonreactive methoxyl groups.

The component parts of the titration curve of silk fibroin have been interpreted in terms of the composition of this protein. Thus the hydroxyl groups of tyrosine appear to bind base as shown by the fact that the base-combining capacity is much greater than can be accounted for by the other groups which are able to bind base.

The presence of free carboxyl groups in silk fibroin is suggested by the shape of the titration curve. From the maximum amount of acid bound an estimate of the total content of free amino groups may be obtained. The effect of added salt is similar to that obtained with other insoluble proteins, namely to increase the quantity of acid or base bound at a given pH, in a manner which suggests that the combination of hydrogen ions is affected by the concentration of anions as well as by the concentration of hydrogen ions and that combination with hydroxyl ions is affected by the concentration of cations.

* Research Associates at the National Bureau of Standards, representing the Textile Foundation.

Introduction

MANY of the chemical and physical properties of a protein fiber are intimately related to the number and arrangement of those groups which bind acid or base. A study of the combination of acid and of base with silk fibroin was therefore undertaken as part of an extensive program for the investigation of the acidic and basic nature of textile fibers.

The manner in which the titration curves of the insoluble proteins, and especially of wool, differ from those of the soluble proteins has been discussed by Speakman and Hirst,[1] by Lloyd and Bidder[2] and, more recently, by Steinhardt and Harris.[3] The titration of silk fibroin is, in some respects, similar to the titration of wool, but differs in other respects because of decided differences in the number and kinds of constituent amino acid residues. The published analyses of silk[4] indicate that fibroin contains relatively small quantities of the dibasic amino acids, arginine, lysine and histidine, all of which would be expected to bind acid, and an appreciable quantity of one diacidic amino acid, tyrosine, which would be expected to bind base unless its phenolic hydroxyl group is blocked in some way.

The data for proteins do not provide an unequivocal indication of the availability of the hydroxyl groups of tyrosine for binding base. Recent work, however, on the reaction of diazomethane with silk and a number of other proteins indicates that the hydroxyl groups of tyrosine in these substances are probably free.

The relatively high content of tyrosine in fibroin made it seem probable that the rôle of the hydroxyl groups in acid-base equilibria would be revealed by consideration of the titration data. Since the methylation of these groups can now be readily brought about,[5] a comparison of the titration curves of untreated and of methylated fibroin should indicate even more clearly the part taken by the phenolic hydroxyl groups in the binding of base by fibroin.

Experimental Procedure

1. Materials

(*a*) *Fibroin*

Raw white Japanese silk which had not been previously treated except for the reeling operation was extracted for 48 hours with alcohol and for 24 hours with ether, both at room temperature, and was finally washed in water. The silk was degummed by treatment with a commercial enzyme preparation, Enzo.* The degumming bath contained 5 g. of Enzo per liter and was maintained at a temperature of 65° C. The ratio of silk to solution was about 1: 40. Each lot of silk was given three consecutive treatments of half an hour each with constant agitation; after each treatment the silk was quickly rinsed in boiling water and was then thoroughly washed in water at room temperature. In order to assure complete degumming it was found necessary to prevent the silk from becomming tightly matted. Determinations of loss of weight showed that three treatments of half an hour each and subsequent washings were sufficient to bring the material to constant weight. The loss of weight on degumming corresponded to the loss reported by Rutherford and Harris[6] for silk of the same lot degummed by boiling in soap solutions.

* Thanks are due the Wallerstein Laboratories, New York, N. Y., for the enzyme preparation used in this work.

(*b*) *Methylated Fibroin*

Fibroin was methylated with diazomethane as described by Rutherford, Patterson and Harris.[5] Analysis of the samples for tyrosine by the method of Lugg[7] showed that the tyrosine content had been reduced from 12.0 to 2.3 per cent, and analysis for methoxyl groups by the method of Vieböch and Brecker[8] showed that the methoxyl content was 2.37 per cent.

2. Methods

(*a*) *Correction for ash*

The degummed silk contained some base, already bound, and yields an alkaline ash. This alkali affects the extent to which acid or base is sorbed from the solution by the fibroin. The hydrogen ion equivalence of the ash was determined by an electrodialytic method which has been described elsewhere.[9] The degummed and washed fibroin had an ash content of the order of 0.1 milliequivalent per gram (*M*-eq/g). In order to reduce the ash content to a lower value the fibroin was electrodialyzed for 24 hours. By this means the hydrogen ion equivalence of the ash was reduced to 0.01–0.02 *M*-eq/g. The titration data were corrected for the effect of this residual ash by subtracting the hydrogen ion equivalence of the ash from the experimentally determined quantity of acid bound, or adding it to the quantity of base bound.

(*b*) *Determination of Moisture*

All the samples were conditioned at 21° C and 65 per cent relative humidity before weighing. The moisture content of the fibers was determined by drying representative samples for 2 hours in a vacuum oven at 105° C. All titration data in this paper are expressed as milliequivalents of acid or of base per gram of dry fibroin.

(*c*) *Correction for Sorption of Water*

In the determination of the titration curves of hygroscopic fibrous materials some investigators have considered the total moisture content of the sample of fibers, at the moment immediately preceding immersion in the solution, as a quantity which should be added to the free water of the system. That is to say, all the water in the system, including that introduced in the fiber phase, has sometimes been regarded as being available for dilution of the solute. However, many workers have recognized, on the basis of direct experimental evidence, that the concentration of an aqueous solution of a solute which is not bound to the fiber by strong chemical or physical forces is *increased* when a sample of fibers of low moisture content is introduced into the solution. Presumably such an increase in the concentration of the solution is due to the selective sorption of water by the fibers. It is also assumed that such sorption effects occur in solutions of acids and bases and decrease the quantity of water which is available for dilution of the acid or base. Since the acid and base binding capacities, as determined in the present investigation, are calculated from changes of titer and since the change in the titer of the solutions will depend upon the selective sorption of water as well as upon the quantity of acid or base bound a correction must be applied for the sorption of water.

The manner of applying this correction term is discussed in detail by Sookne and Harris.[10] In the present investigation the extent of selective sorption of water was investigated by a polarimetric method. The highly optically active disaccharide trehalose was used as a reference substance. It was assumed that the trehalose was not sorbed by the fiber. A weighed quantity, 5 g, of fibroin of known moisture content was immersed in the smallest convenient volume, 60 ml, of trehalose solution, which was 0.05 *N* with respect to hydrochloric acid, and then placed in the constant temperature bath at 0° C. After 24 hours, aliquots were withdrawn from the stock solution and from the solution in equilibrium with the fibres and the rotations were measured in a saccharimeter at 20° C. The rotations of the original and of the final solutions were compared and the difference was interpreted as a measure of the increase of the concentration of the solution with respect to trehalose, which resulted from the sorption of water by the fibroin. The mean result for a pair of duplicate determinations is shown in Table I.

TABLE I

Selective sorption of water by silk fibroin

Dry weight of fibroin	4.57 g
Moisture content per gram of dry fibroin	0.095 g
Change in rotation of solution	1.26%
Original volume of solution	60.0 ml
Water selectively sorbed	0.75$_6$ g
Water selectively sorbed per gram of dry fibroin	0.16$_5$ g
Total water in fiber not available for dilution of solute (grams per gram dry weight)	0.26 g

(d) Titration with Acid

Samples of fibroin weighing either 3.00 or 4.00 g and containing about 9.2 per cent of moisture were placed in 100-ml portions of acid solutions at 0° C. The solutions contained either varying amounts of hydrochloric acid alone or varying amounts of potassium chloride and hydrochloric acid so adjusted as to bring the total ionic strength, at equilibrium, to 0.2 *M*. Aliquots of the original solutions and of the solutions which had come to equilibrium with the fibroin were titrated with standard sodium hydroxide solutions, using bromcresol purple as the indicator. The change in titer together with the dry weight of the sample and the correction for selective sorption of water permits the calculation of the quantity of acid bound per gram of dry fibroin.

To determine whether sufficient time had been allowed for the attainment of equilibrium and whether appreciable acid hydrolysis had occurred, aliquots were withdrawn from the acid solutions which had been in contact with the fibroin for periods of 2, 3 and 4 days. The results indicate that equilibrium is attained within 48 hours and that no appreciable hydrolysis occurs within four days at 0° C in solutions up to 0.1 *N* with respect to hydrochloric acid.

(e) Titration with Base

Titrations with base were carried out in a manner analogous to the method used for acid titrations, with the addition of precautions to prevent

errors resulting from exposure of the solutions to atmospheres containing carbon dioxide. The alkaline solutions were made up from a stock solution of potassium hydroxide of very low carbonate content and a stock solution of potassium chloride of very low carbon dioxide content, by dilution with freshly boiled distilled water.

To determine the time required to attain equilibrium and to investigate the question of the alkaline hydrolysis of the protein material, a number of samples were immersed in potassium hydroxide solutions at pH 12 for various periods of time. The results indicate that equilibrium is attained in about 24 hours at 0° C and that no appreciable hydrolysis seems to have occurred within 72 hours at this temperature, as the quantity of base bound reached a constant value and the Nessler test did not reveal the presence of any nitrogen in solution. In all subsequent experiments the samples were allowed to remain in the solution for 48 hours before aliquots were withdrawn for titration.

(*f*) *Determination of pH*

The pH values of the solutions were determined with a glass electrode following the method used by Steinhardt and Harris.[3]

(*g*) *Temperature Control*

The solutions were maintained at a temperature of 0° C by immersion in a refrigerated bath containing water and ice.

Results and Discussion

The amounts of hydrochloric acid and of potassium hydroxide bound by fibroin at 0° C at different pH values (at equilibrium) are given in Table II and are shown graphically in Figure 1. The titration curve for hydrochloric acid in the absence of salt (open circles) drops steeply from a maximum of about 0.13 *M*-eq/g near pH 1 and appears to reach the base line at about pH 3.9. It should be noted that because of the shallow slope of the curve as it approaches the base line any error in the ash correction or in the titration data will affect the position of the point at which combination with acid appears to begin.

In solutions of chloride ionic strength 0.2 (half-filled circles) acid combination appears to begin at about pH 4.8. The effect of keeping the chloride ion at constant ionic strength 0.2 is clearly indicated by the figure. At the lower values of pH the curves tend to join each other, as indeed they must if the curve for constant ionic strength be extended to that point at which no salt is present. As in the case of wool,[3] the central portion of both the acid and the alkaline regions of the curve for solutions of constant ionic strength is not as steep as the curve for solutions without salt, and a greater amount of acid or base is bound at a given pH. The effect of the presence of salt on the slope and position of the titration curve is greater than could reasonably be accounted for by the influence of the salt on the dissociation constants of the groups which are titrated. It will be observed that for the preservation of electrical neutrality in the solutions and in the fibers it is necessary that the fibers should bind an anion with every proton and a cation with every hydroxyl ion. A few determinations of the chloride titer of the acid solutions served to indicate that chloride

TABLE II

Amounts of acid and base bound by silk fibroin at 0° C

No salt present

pH	Acid bound *M*-eq/g	pH	Base bound *M*-eq/g
1.083	0.132	9.01	0.033
1.131	.130	9.63	.034
1.553	.117	10.40	.052
2.046	.091	12.18	.147
2.331	.074	12.43	.205
2.468	.044	12.76	.314
2.950	.031	13.10	.395
3.522	.003	13.61	.798
		14.25	.904

Ionic strength 0.20

pH	Acid bound *M*-eq/g	pH	Base bound *M*-eq/g
1.187	0.136	9.10	0.070
1.822	.119	10.61	.139
2.101	.115	11.44	.228
2.360	.092	11.80	.298
2.875	.080	12.24	.487
3.138	.077	12.44	.581
3.276	.057	12.89	.686
3.968	.049	13.48	.767
4.633	.001		

ions are bound in quantities approximately equivalent to the amount of hydrogen ion bound. A detailed discussion of the effect of salt and a theoretical treatment of the titration data for another fibrous protein, wool, have been given elsewhere by Steinhardt and Harris,[3] who showed that the quantity of acid bound depends upon the concentration of anions as well as on the concentration of hydrogen ions and that the quantity of base bound similarly depends on the concentration of cations as well as on hydroxyl ions. They explained the direct dependence on anion, or cation, concentration on the basis of the assumption that when the protein combines with hydrogen ions it also forms partially dissociated stoichiometric complexes with anions and when it combines with hydroxyl ions it forms similar complexes with cations. These conclusions now appear to be applicable to silk fibroin as well.

The titration curve for fibroin obtained from these experiments at 0° C differs in several respects from that given by Lloyd and Bidder.[2] At the higher concentrations of acid Lloyd and Bidder indicate that rapidly and continuously increasing amounts of acid are bound as pH decreases, the highest value shown being some 0.3 *M*-eq/g at pH 1; the data of the present investigation tend toward a maximum of about 0.13 *M*-eq/g in the region of pH 1. This difference cannot be ascribed to the effects of ash because Lloyd and Bidder report an ash content of only 0.02 per cent which, on the assumption of an equivalent weight of 40 for the ash, as found in the fibroin used in the present investigation, would amount to about 0.005 *M*-eq/g. The discrepancy may be due in part to some decomposi-

tion of the fibroin at the higher temperatures at which Lloyd and Bidder worked. The alkaline branches of the curves are less dissimilar and in this case at least a part of the difference may be attributed to a temperature effect. It has been shown that temperature appreciably influences the binding of base by wool but has very little effect on the binding of acid.[11]

It is recognized that the acid- and base-combining capacities of proteins may usually be correlated with their contents of diacidic and dibasic

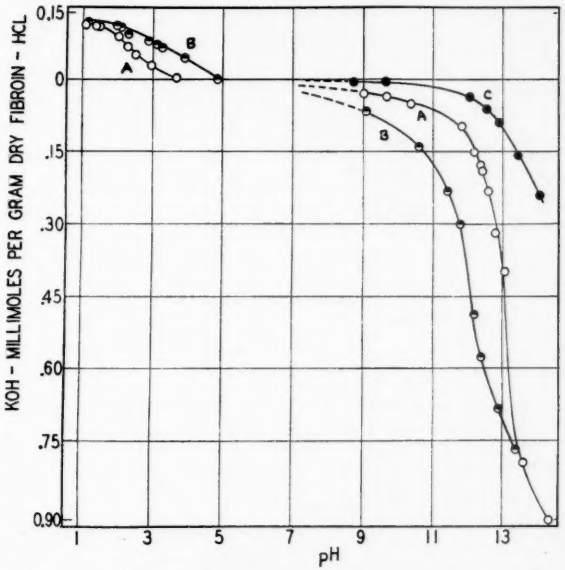

Fig. 1. Titration curves of silk fibroin with hydrochloric acid and potassium hydroxide.
A—No salt
B—Ionic strength 0.2 *M*
C—Methylated fibroin, no salt

amino acids.[12] The published analytical data on the composition of fibroin are given in Table III.[4, 13] The maximum quantity of acid bound by fibroin, 0.13 *M*-eq/g, is nearly twice the sum of the reported content of arginine and lysine. Such a discrepancy is not unexpected since in the isolation of small quantities of amino acids from protein hydrolysates the analytical results invariably are low.

In the literature no values whatever are reported for dicarboxylic acids in silk fibroin. The nature of the titration curve, however, is such as to suggest that dicarboxylic acid residues are probably present. The total amount of acid plus base bound between pH 1 and pH 7–8 (in which range the —COOH groups are known to undergo dissociation), which is not less than 0.13 and may be as much as 0.17 *M*-eq/g in the case of silk fibroin,

TABLE III

Amino acid composition of fibroin

Amino acid	Percent	*M*-eq/g
1) Glycine[a]	43.8	5.84
2) Alanine[a]	26.4	2.97
3) Tyrosine[a]	13.2	0.73
4) Arginine[a]	0.95	0.055
5) Lysine[b]	0.25	0.018
6) Histidine[b]	0.07	0.005

[a] *Reference* [4].
[b] *Reference* [13].

may be regarded as a measure of the total number of free carboxyl groups in the protein. Previous evidence that silk fibroin contains free carboxyl groups was given by Rutherford, Patterson and Harris,[5] who infer the presence of about 0.2 *M*-eq/g of free carboxyl groups in the untreated fibroin from the analyses of methylated fibroin for unmethylated tyrosine and for methoxyl groups. The latter estimate lends support to the interpretation of the quantity of acid plus base bound between pH 1 and 8 as representing the free carboxyl content of fibroin.

The amount of base bound in the strongly alkaline region, that is at pH greater than 11, greatly exceeds the content of free carboxyl groups and can be accounted for only by postulating that the phenolic groups of the tyrosine take part in the binding of base. This result is not unexpected, as Rutherford, Patterson and Harris [5] concluded on the basis of their study of the methylation of fibroin with diazomethane that the hydroxyl groups are free. The greatest amount of base bound in the range covered by this investigation, 0.90 *M*-eq/g, is somewhat more than the tyrosine alone would account for and is, fortuitously, equal to the tyrosine content plus the estimated content of free carboxyl groups. Presumably higher amounts of base would be bound at higher pH values at which, however, the estimation of base bound and of pH would be attended by such large errors as to make the experimental data unreliable.

Additional evidence for the conclusion that the phenolic hydroxyl groups of tyrosine bind base is provided by the data on the titration of methylated fibroin with potassium hydroxide, given in Table IV. In this material all but approximately one-fifth of the tyrosine had been methylated. The ti-

TABLE IV

Amounts of base bound by methylated fibroin at 0° C

pH	Base bound *M*-eq/g
8.74	0.005
9.48	.005
12.15	.037
12.55	.061
12.84	.091
13.47	.166
14.14	.283

tration curve (solid circles, Figure 1) is shifted toward higher pH. Up to pH 9.5 very little base is bound and at any given pH the amount bound is very much less than in the case of the unmethylated fibroin. This greatly decreased base-binding capacity of the methylated fibroin lends support to the interpretation of the very steep portion of the curves for nonmethylated fibroin as being due to the titration of the phenolic hydroxyl groups of tyrosine.

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Fundamental Properties of Textile Wastes. IX. Concentration of Sulfur Black Dyes by Froth Flotation

By L. C. SURPRENANT, J. E. MAGOFFIN, and F. K. CAMERON

A Textile Foundation Publication

Abstract

In a previous paper[4] in this series, it was shown that, in general, flotation of colloidal material is improved when the electrokinetic potential of the particles is lowered and flocculation results. Similarly, the agglomerated state has been found necessary for satisfactory flotation of minerals. The work reported here is a comprehensive study of the flotation of sulfur black dye, including the effect of concentration of dye and of various electrolytes on the process. The apparatus used was that described by Clanton, Cameron, and Magoffin.[4] Migration velocities of the flocculated dye were measured by the microscopic method, using the improved cell suggested by Moyer.[6] The dyes investigated are registered under trade names. Sulfogene Carbon MCF is a product of E. I. duPont de Nemours & Co., Inc. Sodysul Black RACF was obtained from the Southern Dyestuff Corporation and is described as a solution of sulfur black with sodium sulfide and carbonate.

Part I

THE relations between electrokinetic potential and success of flotation have not been widely studied, although a few investigators have been interested. Bull and coworkers[2, 3] determined the effect of various cations on the migration velocity of galena, and in turn the effect of this on the flotation of galena by eucalyptus oil. Those cations which lowered the migration velocity the most were the worst poisons for this flotation, which is contrary to the results obtained more recently by Magoffin and Clanton[5] and Clanton, Cameron, and Magoffin[4] for the flotation of colloids. The variance is probably due to the different types of floating agents used in the two investigations.

The dyes were dispersed in relatively concentrated master sols, from which the suspensions actually studied were prepared by dilution.* † In general the meager sol contained all the reagents found in the final suspension with the exception of the reagent whose influence was being studied.

* The dyes were analysed using a variation of the methods of Zänker and Schnabel[9] and Ossipov.[7] The Sulfogene carbon MCF analysed 68.6% pure dye and the Sodysul black RACF, 22.8%.

† Tap water was used in all experiments. The dispersions were prepared according to manufacturer's directions, the additional electrolytes being added after the dye was in solution.

This reagent was added after dilution. The suspensions were prepared in a seven liter conditioning jar and agitated for fifteen minutes to insure complete dispersion. The reagent being studied was added in water solution and the mixture agitated for fifteen minutes more, after which time a five hundred cc sample was withdrawn for pH and migration velocity measurements. The remaining six and one-half liters were transferred to the flotation cell and the floating agent added. In most experiments reported a 1 percent solution of DP 243 * was the agent used. This was added in two cc portions at two minute intervals, with the exception of the first addition of five cc. Additions of floating agent were continued until flotation was complete or had ceased. The manner of addition of other floating agents, used in some experiments, is noted under the discussion of the experiments.

The froth was usually stable and voluminous at the beginning of the run, becoming less so as the flotation progressed. It was allowed to overflow from the cell into a bucket, and after a sufficient settling time, the volume was measured. As a rule, the effluent was water white.

The change of pH, from original suspension to effluent, was measured in all cases. Migration velocity measurements were possible only on the suspensions of 0.1 gm. dye per liter or less.

Before studying the effect of various electrolytes on the migration velocity and flotation of dye, the effect of the DP 243 was determined. Since this agent is a quaternary ammonium salt, it should lower the negative electrokinetic potential of the dye particles, and eventually cause flocculation. This was found to be the case, see Fig. I. This action is an

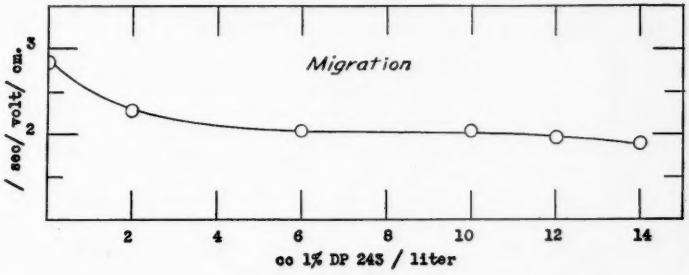

Fig. I

important contributing factor in the successful flotation of sulfur black with this agent.

Waste liquors from sulfur dye processes usually contain dye, sodium sulfide, sodium carbonate or sodium hydroxide, sodium chloride or sodium sulfate, wetting agents, and possibly other electrolytes. The relative amounts of these substances present will be an important factor in the success of any treatment process. To determine their importance in flotation, a systematic study was made of the effect of each of these substances on the migration velocity and floatability.

The influence of sodium carbonate and sodium hydroxide was deter-

* A cationic wetting agent made by E. I. du Pont de Nemours Co.

mined on a suspension containing dye, sodium sulfide, and varying concentrations of the alkali under study. Results are shown in Fig. 11. The similarity of the two curves, and the close resemblance of the migration velocity curves to curves for like studies on other hydrophobic sols, indicate that the influence of these two electrolytes is due primarily to their control of the hydrogen ion concentration of the system. The increasing alkalinity of the system tends to stabilize the dispersion of the dye particles and flotation is more difficult and less complete.

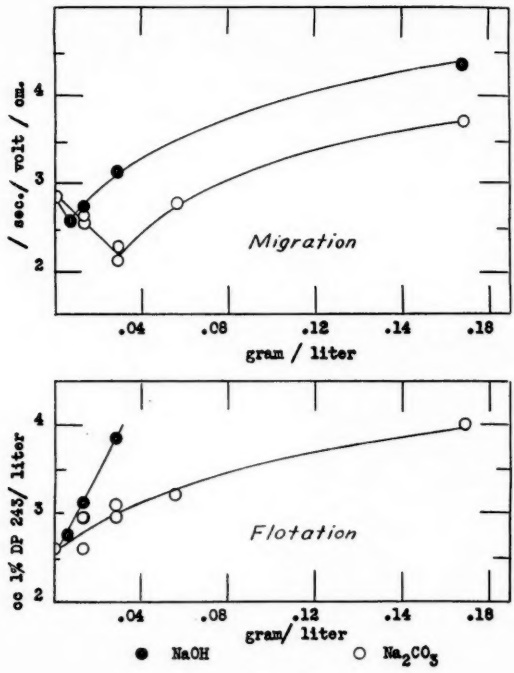

Fig. II

Another important electrolyte found in sulfur dye waste liquor is sodium chloride, which is used to salt out the dye toward the end of the dyeing run. The ratio of this salt to the dye and its effect on the flotation of the dye may be very important. (Starting with a solution of 20 gms to the liter, the concentrations after dilution of 35 cc to seven liters were dye 0.1, Na_2S 0.07, and Na_2CO_3 0.014 gram per liter.) As will be seen in Fig. III, increasing concentration of sodium chloride affects the migration velocity but little, but does improve flotation, flocculation taking place at a concentration of 0.62 gm. per liter. As has been shown previously, flocculation is a definite aid to flotation. As a rule it is accompanied or caused

by a reduction in migration velocity, which is not the case with sodium chloride. Perhaps this accounts for the fact that the improvement in flotation is somewhat less than is obtained when certain other electrolytes are used for the flocculating process.

The use of flocculating electrolytes to improve the flotation of colloidal suspensions was suggested by Clanton, Cameron, and Magoffin[4] but no extensive and systematic study has been made. For use with the sulfur dyes

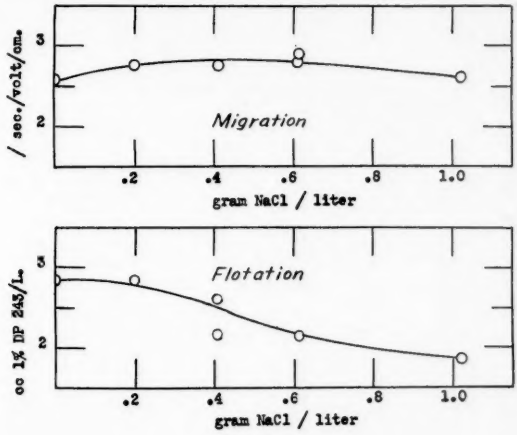

Fig. III

under investigation, the following electrolytes were chosen: sulfuric acid, calcium chloride, ferrous sulfate, ferric chloride, and aluminum sulfate. The electrolytes were added to the suspension in water solution while the system was being agitated vigorously. The master dye sol used for these experiments contained, in addition to sodium sulfide, sodium carbonate and sodium chloride in approximately the ratio to dye in which they are found in actual waste liquors. The final concentrations after dilution to seven liters were:

Dye	0.10 gram/liter
Na_2S	0.07
Na_2CO_3	0.014
NaCl	0.20

The data for the migration velocity and flotation of sulfur black as affected by the flocculating agents is plotted in Figures IV and V. All of the electrolytes used reduce the migration velocity, flocculate the dye, and improve the quality of flotation within 30 minutes. In each case there is an optimum concentration or concentration range for best flotation, too much of the electrolyte having a deleterious effect. This optimum range begins at the concentration where flocculation of the dye is first noticeable to the eye.* Flotation was best with sulfuric acid as flocculating agent.

* Flocculation occurred at the following concentrations of electrolytes: H_2SO_4 0.097 gm/L., $CaCl_2$ 0.04 gm/L., $FeSO_4 \cdot 7H_2O$ 0.032 gm/L., $FeCl_3 \cdot 6H_2O$ 0.027 gm/L., $Al_2(SO_4)_3 \cdot 18H_2O$ 0.071 gm/L.

The effluent was water white, and the froth quite concentrated. Calcium chloride was the least effective, both in flocculating power and in improving flotation.

The flocculating action of electrolytes on sulfur dyes falls into two types: straight neutralization of the negative potential on the dye particles by positive ions or micelles, and de-peptization. De-peptization may be defined as the stripping of the peptizing ions from the stable dye particle, thus causing agglomeration. De-peptization may also take place through oxidation of the sulfide ion, the peptizing ion, to sulfate, which

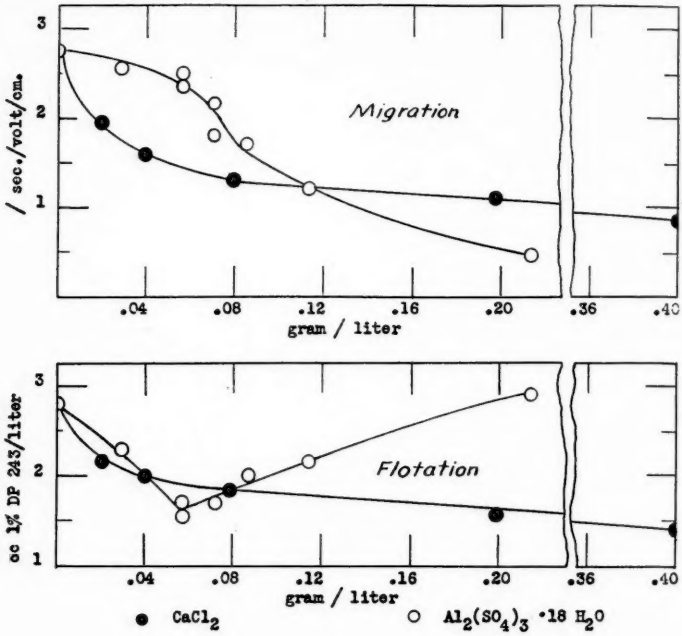

Fig. IV

has no peptizing action. This last, is usually the method used to precipitate the dye in the manufacturing process, and is the cause for a good part of the ash content of raw dye. Salting-out of the dye by the electrolyte is another possibility, particularly in industrial operations.

The action of sulfuric acid is one of de-peptization, the sulfide ion being removed from the system as hydrogen sulfide. The same effect was obtained by bubbling carbon dioxide gas through the suspension,* since carbonic acid is a stronger acid than hydrogen sulfide. Sulfur dioxide is not effective, because the dye is peptized by sulfite ions.

* Belenky [1] precipitated a sulfur dye with CO_2 as a means of purification of the dye for laboratory investigations.

Aluminum sulfate and ferric chloride owe part of their flocculating power to de-peptization, because of the acid character of their aqueous solutions. However, part of the flocculating action of these is due to neutralization of the potential of the dye particle by the highly positive cations. With calcium chloride and ferrous sulfate the flocculation is caused entirely by neutralization.*

The difference in the type of flocculating action of these electrolytes undoubtedly accounts, in a large part, for their different degrees of effectiveness in improving flotation. Sulfuric acid is by far the most effective, aluminum and ferric iron are fair to good, while ferrous iron and calcium are fair.

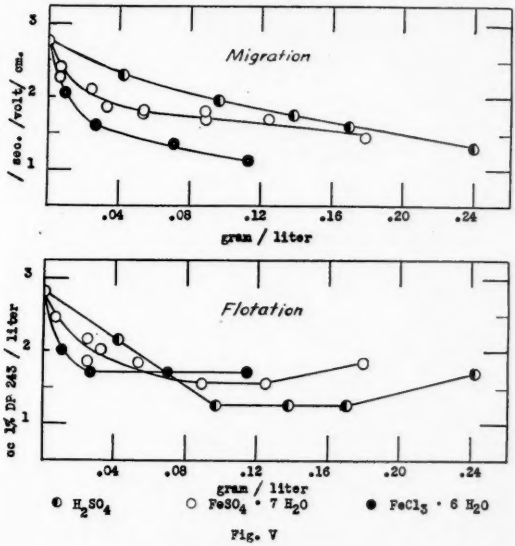

Fig. V

Fig. VI is a plot of the migration velocity and flotability against pH of the solutions. The pH variations were brought about by the addition of the electrolytes noted. Considerable differences are noted in the migration velocity curve, but the floatability for comparable pH is close for all the electrolytes. The effect of pH seems to be important with DP 243 as a flotation agent. In line with this are the findings of Wark and Wark[8] that in mineral flotation with amines the adsorption of the amine is greater at the lower pH. The process of flotation always changed the pH toward the neutral point.

Depending upon the amount of wash water used, the concentration of dye and electrolytes in waste liquors will vary over a wide range. The suspensions already discussed represent the lower limit, while the upper limit is probably about 6.0 gram dye per liter. Thus, a complete picture of

* Dr. R. E. Rose disagrees with this statement, pointing out possibilities of oxidation or of salting out effects.

concentration by flotation must include studies on more concentrated suspensions than hitherto discussed. The Sulfogene Carbon MCF dye was studied at a concentration of 1.0 gram per liter and the Sodysul Black RACF dye at concentrations of 0.69 * and 2.07 grams pure dye per liter. The master sols were again prepared so that the ratio of electrolytes to dye was the same as that found in actual waste liquors. The suspensions were prepared in the same manner as before, save that the conditioning time was lengthened to one hour. After transference to the flotation cell, the DP 243 was added as before, the first two additions being ten and four cc respectively.

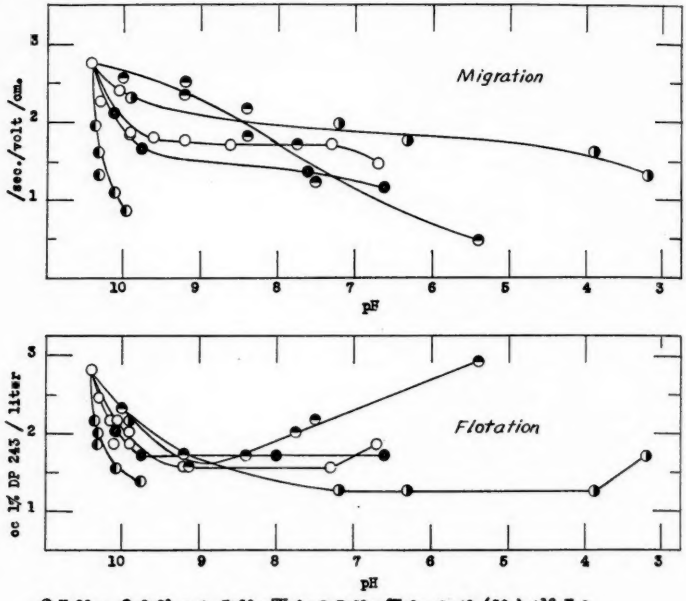

Fig. VI

The results of the studies on both dyes are given in Fig. VII. Without the addition of flocculating electrolytes the flotation is incomplete and inefficient. With sulfuric acid, aluminum sulfate, and ferric chloride the flotation of both dyes was improved, although after complete flocculation of the dye is assured, further addition of electrolyte has no appreciable effect. If too large an excess is added, the floatability is impaired. Ferrous sulfate improves the flotation of the Sulfogene Carbon MCF somewhat, but is quite

* This represents the same amount of pure dye as 1.0 gram per liter of raw Sulfogene dye. The dye was brought into solution by boiling in water a mixture of dye, 7 parts, sodium sulfide 5 parts and sodium carbonate 2 parts, approximately.

ineffective with the Sodysul Black RACF. Again the best flotation was obtained when sulfuric acid was the flocculating electrolyte.*

The conductivity of these concentrated suspensions is so great, that migration velocity measurements are impossible. Thus correlation of floatability and electrokinetic potential cannot be made. It may be assumed, however, that the potential is lowered in much the same manner as in the case of dilute suspensions, and that part of the increased efficiency of flotation with flocculation is due to this lowering.

Flotation of the 0.69 gram per liter Sodysul Black RAFC was attempted with several pure amines that became available at this time. Butyl, dibutyl, and octyl amines were tried with but little success. Dioctyl amine, however, was very effective, particularly in the low pH range, as is shown

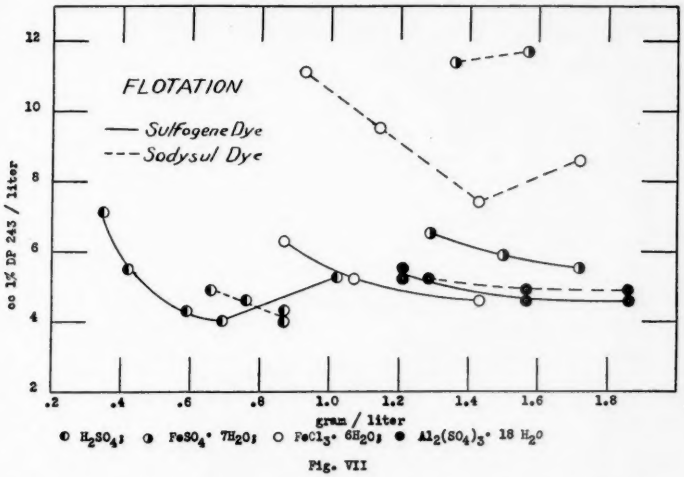

Fig. VII

by the data in Table I. Potassium ethyl, and potassium isoamyl xanthates, in 1 percent solutions, were also found to be effective. It was necessary to use five drops of Yarmour Pine Oil No. 302 with the xanthates in order to maintain a stable froth.

The highest concentration of dye studied was 2.07 gram dry weight per liter, using Sodysul Black RACF. Sulfuric acid was the only flocculating agent used, since it has been shown to be the best, by far, in the studies on the lower concentrations. The results are given in Table II. For the medium concentration of Sodysul Black RACF, using H_2SO_4 as conditioning agent, the volume of material floated from one liter of sol was 46 cc, while for the highest concentration (Table II) the best result was from one liter to 216 cc. Most of the dye is removed in the first stages of flotation, the last few per cent is almost impossible of removal.

The concentration of dye in the suspension is very important to the

* That these dyes showed real differences in their responses to flotation treatments may be surprising. Dr. Rose points out that they are supposed to be essentially identical.

Table I

Effect of H_2SO_4 on Flotation of "Sodysul" Dye (0.69 gm./L.) Using a Secondary Amine and Xanthates as Flotation Agents

Conc. H_2SO_4 gm./L.	pH Start	Vol. Flotation Agent/Liter Milliliters	Vol. Concentrate per Liter Treated Milliliters	Effluent	
				pH	Approx. Removal Dye %
Dioctyl Amine					
0.49*	7.45	—†	—	9.1	Trace
0.61*	6.50	0.18	79	8.0	94
0.75*	3.17	0.06	77	4.17	96
0.90*	2.80	0.06	120	3.0	96
0.90*	2.75	0.05	120	3.1	94
1% Potassium Ethyl Xanthate					
0.49*	7.6	14.6	115	3.60	80
0.90*	2.85	7.5	150	9.35	96
1% Potassium Isoamyl Xanthate					
0.49*	7.5	5.4	115	9.25	93
0.68*	6.0	5.7	115	7.6	94
0.90*	2.8	3.8	77	3.2	96

* Dye flocculated.
† Trace flotation even with large amount of flotation agent.

Table II

Effect of H_2SO_4 on Flotation of "Sodysul" Dye (Conc. 2.07 gm./L.)

Conc. H_2SO_4 gm./L.	pH Start	Vol. 1% DP 243 per Liter Milliliters	Vol. Concentrate per Liter Treated Milliliters	Effluent		
				pH	Color	Approx. Removal Dye %
1.63†	8.55	11.4	308	9.47	Trace Green	98
2.08†*	7.15	8.9	216	8.75	" "	"
2.43†*	3.95	7.5	231	6.38	" "	"

† Dye flocculated.
* Blown-out with air before flotation. pH after equaled 9.11 and 6.55 respectively.

success of flotation. With increasing amount of dye the degree of concentration obtained by flotation is lowered, and the froth carries over more liquid. There is an improvement in the ratio of floating agent to dye required, but in general flotation is better with the more dilute suspensions.

Actual waste liquors obtained from a Greensboro, N. C. mill were clarified by froth flotation using sulfuric acid and carbon dioxide as flocculating agents and DP 243 as floating agent. Results comparable to those described above were obtained, although frothing was a little more voluminous owing to the presence of wetting agents in the waste liquors.

Part II

Frequently the transition from small batch to larger scale continuous operation results in improvement in process and yield. For this reason, continuous flow flotations were studied on a somewhat larger scale than hitherto described.

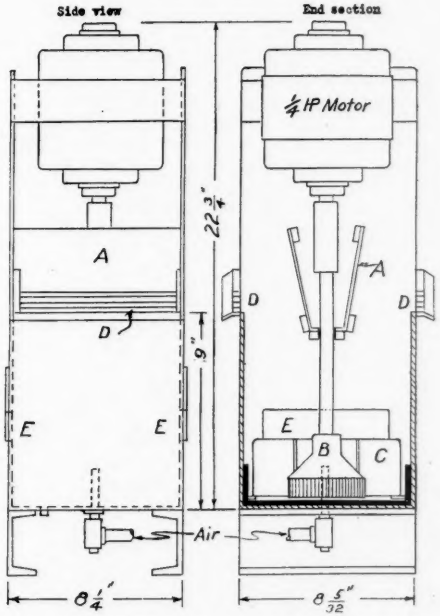

Fig. VIII. Agitair Flotation Cell.

A six cell experimental Agitair unit made by the Galigher Co., Salt Lake City, Utah, was used for this work. The cells, Fig. VIII, are of the air-agitator type, similar to the one previously described. Air is admitted through the bottom of the cell into the cone of the direct-driven agitator

(B). This runs at 1725 RPM and has a ring of vertical prongs on its bottom edge, through which the air passes. The rapid rotation breaks the air stream into many small bubbles which are thrown into contact with the solid particles suspended in the liquid.

Radial stainless steel baffles (C) confine the agitation to the lower half of the cell, minimizing the turbulence in the upper region. The slurry enters at (E) below the liquid level and leaves at a similar opening at the opposite side of the cell. Froth baffles (A) are provided to deflect the froth to the overflow weirs (D). Removable stainless steel weir bars are used to control the froth level, while a similar arrangement in the weir box at the outlet end of the unit controls the liquid level. The agitator and cell bottom are covered with rubber to lessen abrasive effects.

The six cells were connected in series for all of the experiments conducted. A weir box, fitted with removable outlet nozzles, placed at the inlet to the first cell permitted control of the rate of flow through the unit. Using a constant level in this weir box and four different nozzles, rates of flow of 1.3, 2.2, 4.2, and 7.2 liters per minute were obtained.

One hundred gallon drums, fitted with variable speed "Lightning" mixers, served as conditioning tanks. From these the slurry passed through the weir box, regulating the rate of flow, to the first cell, and by connecting openings through each of the remaining cells of the unit. Froth overflow was caught in inclined troughs, which conducted it to a receiving drum. The clarified liquor, when desired, was also caught in a receiving drum, from which it could be returned to the apparatus for re-treatment. Air was supplied to the flotation cells, through a manifold, by a Root-Connersville blower at approximately one and one-half pounds pressure.

The dye suspensions were prepared in the large drums in the following manner: dry sodium carbonate was dissolved in approximately 95 gallons of water, the liquid dye Sodysul Black RACF added with agitation, and after ten minutes, the dry sodium chloride. Ten minutes more agitation was assumed to be sufficient for complete mixing and dispersion. After this time the flocculating agents were added in water solution, the drum filled to the 100 gallon mark, and the mixture agitated for thirty minutes to one hour. This much conditioning time was found to be necessary to assure uniformity in the slurry. After conditioning, the entire amount of floating agent to be used was added and the agitation cut down to a minimum. It was necessary to add the floating agent in this manner as no satisfactory means for proportioning it directly into the cells was available.

In general 100 gallons were used for each flotation, although in eseveral cases smaller volumes were used. Fifteen gallons were run through the system each time before any data was taken to be sure that the unit was operating satisfactorily. The liquid and froth levels were adjusted by means of the weir bars as the flotation warranted, the average levels being 6.5 and 3 inches respectively.

Only Sodysul Black RACF was used in these experiments, because of the ease with which the suspensions can be prepared, and since it has already been shown that results obtained with it and with the dry dye are approximately the same. Sulfuric acid was used as the flocculating agent, because of its proved superiority over the other electrolytes tried.

The data for the dilute suspensions are listed in Table III and those for more concentrated suspensions in Table IV. Excellent clarifications

TABLE III

Continuous Flow Flotation of "Sodysul" Dye
(Conc. 0.69 gm./L.)

Conc. H_2SO_4 gm./L.	pH Start	Vol. 1% DP 243 per Liter Milliliters	Vol. Concentrate per Liter Treated Milliliters	Effluent	
				pH	Conc. Dye gm./L.
Rate of flow—1.3 liters/min.					
0.53†	6.51	4.2	50	8.15	0.16
Rate of flow—2.2 liters/min.					
0.53†	6.75	2.1	270	8.33	0.5
" †	6.51	4.2	210	8.15	0.4
" †	6.25	6.6	70	8.10	0.1
0.61†	6.5*	2.1	390	7.45*	0.65
" †	7.0*	4.2	130	7.20*	0.2
" †	5.5	6.6	130	7.00*	0.06
0.65†	3.70	2.1	70	6.6	0.4
" †	3.72	4.2	110	5.55	0.1
" †	3.61	6.6	110	7.28	0.06**
Rate of flow—4.2 liters/min.					
0.65†	5.50*	6.6	130	7.12*	0.03
0.83†	2.95	6.6	80	3.50	0.04
Rate of flow—7.2 liters/min.					
0.65†	4.90	2.6	40	7.0	0.4
" †	3.25	4.0	—	4.18	0.06
" †	3.47	5.3	100	6.02	0.11
" †	3.68	6.6	150	5.87	0.03
Rate of flow—2.2 liters/min.					
—	5.75***	2.1	40	6.21	0.03
—	6.28****	1.1	130	6.30	0.005

* pH meter out of order the day these runs were made. Samples stood over weekend before pH was taken.
** This run gave a water-white effluent at start.
*** Recycle of effluent having dye conc. 0.25 gm./L.
**** Recycle effluent from ***. Dye conc. 0.03 gm./L.
† Dye flocculated.

TABLE IV

Continuous Flow Flotation of "Sodysul" Dye
(Conc. 2.07 gm./L.)

Conc. H_2SO_4 gm./L.	pH Start	Vol. 1% DP 243 per 1 iter Milliliters	Vol. Concentrate per Liter Treated Milliliters	Effluent	
				pH	Conc. Dye gm./L.
Rate of flow—1.3 liters/min.					
2.65‡	4.25	7.9	280	7.20	0.26
Rate of flow—2.2 liters/min.					
2.65‡	4.25	7.9	340	7.25	0.16
2.70‡	3.22	5.3	160	7.60	1.12
—	7.5*	2.6	180	7.00	0.40
—	7.25†	2.6	110	7.1	0.06

* Recycle effluent (Approx. Conc. 1 gm./L.).
† Recycle effluent from * (Approx. Conc. 0.3 gm./L.).
‡ Dye flocculated.

were obtained with the dillute suspensions of low pH, flotation being complete, as a rule, in the first three cells. For this reason changing the rate of flow of the slurry had little effect, and clarification at 7.2 liters per minute was as good as at the slowest rate. It is apparent that the amount of floating agent used is very important, and that a sufficient amount must be added. The ratio of floating agent to dye is somewhat larger than that found in the small scale batch flotations, which is probably due to the manner in which it was added to the suspension.

With concentrated suspensions, one processing is not sufficient for complete clarification, regardless of the rate of flow and amount of floating agent. Three successive processings, with additional floating agent, results in good clarification, but the total volume of froth obtained is large. As shown by the batch flotation, best results are obtained with dilute suspensions of a low pH.

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Factors Influencing Flocculation and Precipitation. Influence of Initial Particle Size*

By ELLINGTON M. BEAVERS, JAMES E. MAGOFFIN and FRANK K. CAMERON

A Textile Foundation Publication

Abstract

It has been found that the following properties of flocculated suspensions of bentonite are dependent upon initial degree of dispersion: (a) the shape and form of the floc produced; and consequently, (b) the rate of settling of the dispersed phase through a given distance; (c) the extent to which the particle charge is lowered by a fixed amount of coagulating agent; (d) the adsorbability and solubility effect.

A general equation has been developed for the type of "compression settling" observed here, which has been shown to be applicable to these data.

Some of the physical properties of the suspending media have been studied, and it has been suggested that still other variable factors (possibly changes of surface phase), which should be investigated, have an integral part in the flocculation process.

The various factors studied are discussed as to their influence on flocculation, and previously observed sedimentation behavior of similar suspensions is explainable on the basis of the conclusions drawn.

Introduction

THE purposes of this investigation are (1) to determine the effect of degree of dispersion on the flocculation and precipitation of colloidal suspensions, and (2) to study the fundamental properties of both suspension and medium to obtain a clear view of the controlling factors. The other possible variables in such a study, as set out in a previous paper,[2] are controlled where possible.

The systems selected for this study are suspensions, of various characteristics, of bentonite †—a colloidal clay. Bentonite has been defined as a "natural hydrous aluminum silicate capable of swelling reversibly in water to at least six times its original apparent volume to form a gelatinous mass with the consistency and appearance of grease."[10]

* This investigation was made in part under the auspices of the Textile Foundation, and under the direction of Dr. F. K. Cameron, at the University of North Carolina.

† Wyoming "Volclay," marketed by the American Colloid Company, Chicago, Ill.

It has been well established [6, 7] that the clay adsorbs water very strongly. It exhibits the phenomenon of thixotropy over quite a range of particle sizes and concentration.[8] Bentonite sols in water are negatively charged and have an average pH of about 9, varying with concentration.[3] They are easily prepared, and are very stable and reversible (consequently reproducible), with a minimum of aging effects.

Some aspects of the sedimentation problem with bentonite have been studied. Coward,[4] in 1924, by following the boundary between suspended material and supernatant liquid, found that the settling is more rapid, the lower the concentration. Also, the rate is in a large degree dependent upon the size of the vessels used: "In test-tubes, the sol after coagulation had settled only 18 per cent of the way toward complete clarity after eight days, but there was 36 per cent clearing in only two days in an ordinary 500 c.c. glass measuring cylinder."

Olin and coworkers [9, 10] investigated the uses of bentonite as a coagulant in water treatment, and found that the clay possesses zeolitic activity, particularly in alkaline solutions. Imhoff cones were used to determine the rate of settling and sediment volume of the coagulated suspensions. It was discovered that below a value of nine, pH has no effect on the settling time; above nine, the influence increases rapidly. The results were admittedly poor and require checking.

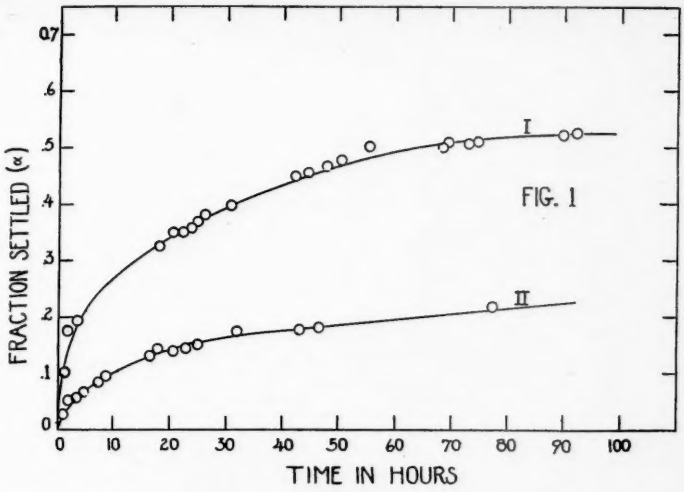
Experimental

The properties of the whole suspension were first studied. In concentrations of about 1%, without added electrolyte, it has a light yellow color and is quite opaque. On standing, a coarse sediment accumulates in a short time, and subsequent settling, still comparatively rapid, builds up a layer of thick, "buttery" material of smaller particles. After six months, a column of the suspension 30 cm. high showed four well-defined zones, the uppermost a clear, greenish-yellow zone about 4 cm. deep, the second a more dense and less translucent zone about 20 cm. deep, the third a still more dense, opaque layer of sediment about 5 cm. deep, and a bottom layer of a reddish-brown sand.

The rate of settling of this suspension was quantitatively studied in the apparatus developed for this investigation,[3] and curve I in Fig. 1 was obtained. From this curve it is apparent that, because of the presence of the coarser material in the suspension, over 25% of the solid has settled at the end of 10 hours, while only 50% has settled at the end of 80 hours.

It was felt desirable to remove these larger particles since they might cause "weighting" or turbulence which would affect the settling of the finer particles with which this study is at present concerned. Filtration either by gravity or suction in a Buchner funnel with coarse filter paper proved infeasible. A two-liter separatory funnel was filled with the suspension and allowed to stand for two hours (as indicated by curve I), at the end of which time the stopcock was opened and the accumulated sediment drained. Curve II in Fig. 1 was obtained with this decanted sol, showing that a large part of the coarser grains had been removed, and, by comparison of I and II, that the larger particles do have some influence on the rate of sedimentation of the remainder of the suspension.

Hauser and coworkers [7] have demonstrated the adaptability of bentonite sols to fractionation by the supercentrifuge. A similar procedure has



been followed here, using a steam-driven Sharples supercentrifuge equipped with different injection nozzles for alteration of the time of retention of the sols in the bowl. By controlling speed and retention time, it has been possible to separate these sols into four fractions of different average particle sizes. (From data presented later in this paper, it is apparent that fractions 2 and 3 differ only slightly.)

Several approximately 4% slurries were prepared by slow addition of 400 gms. of air-dry bentonite (over a period of about 1½ hours) to about 8 liters of redistilled water (specific conductivity, 1.23×10^{-6} mho), with mechanical stirring which was continued for another 1½ hours. At the end of this time, the uniform mixtures were quite viscous and quickly "set" to a thixotropic gel when stirring ceased. This rigidity was easily broken by slight agitation.

These mixtures were fractionated at the speeds indicated in Table I, and if the process were ideal and complete the four resulting dispersions would contain particles within only the indicated size ranges, calculated from a modification of Stokes' law.[6] Actually, no attempt was made to

TABLE I

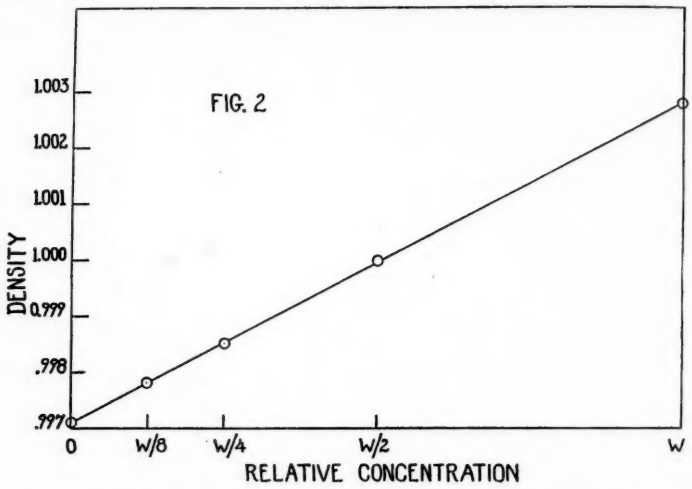
Particle-Size Fractions

Fraction No.	Time to Pass Bowl	Bowl Speed (R.P.M.)	Size Ranges (microns)
1	20 secs.	12,000	>.235
2	20 "	25,000	.235–.112
3	70 "	46,000	.112–.033
4	—	—	<.033

make the separation this sharp, by repeated centrifuging of each fraction; a second treatment was considered to be sufficient for the desired purpose.

The "solid" obtained in each run was diluted with a little water and stored in a closed Pyrex container until use, when it was redispersed by dilution, with stirring. Fraction-4 is the final effluent, with a density of 1.0036, and the concentrations of the other three fractions were brought to the same point. This final fraction is almost clear, and, in general, has the same appearance as the uppermost zone previously described for the whole sol.

The problem of determining and maintaining a constant concentration with all suspensions presented some difficulties. Evaporation and heating in an oven at 110° to constant weight proved infeasible since the process requires 8–10 hours for each sample, and the solid is then so highly hygroscopic that a satisfactory weighing cannot be made. A method based on the suspension density was developed in the following manner. A fairly concentrated sol was prepared and its density determined, after which it was repeatedly diluted, the density being obtained after each addition of a known amount of water. These density values plotted against relative dilution (Fig. 2) gave a straight line extrapolating to the density of water



at infinite dilution. Hence, solution effects are not appreciably altered by concentration, and it is true that

$$\frac{(D_1 - d_m)}{(D_2 - d_m)} = \frac{w_1}{w_2} = \frac{V_2}{V_1} \qquad (1)$$

where D and V are density and volume of suspension containing w grams of dispersed phase.

The use of this formula may be illustrated by an actual case. It was found that 5300 c.c. of a slurry of fraction-1 had a density of 1.0079 at

25°. It was desired to bring this down to the aforementioned value of 1.0036. Substituting in equation (1),

$$\frac{1.0079 - 0.9971}{1.0036 - 0.9971} = \frac{V_2}{5300} \qquad (2)$$

from whence V_2 is 8800 c.c. Hence, 8800–5300 c.c. (3500 c.c.) of water was to be added to the slurry. After this addition, the density was checked and found to be 1.0036. Similarly, a final check density has always been made for each adjustment of concentration, but in every case no further adjustment has been necessary.

By following this procedure the concentration may be held constant, although its absolute value is unknown since the density of the clay particle in suspension is not known with certainty. Assuming the probable value of about 2.75 for the density of the particle, these suspensions are all very nearly 1% by weight.

The density determinations are made by bringing the suspension and pycnometer to temperature separately, before filling, to avoid errors caused by sedimentation within the pycnometer before adjustment of the liquid volume.

The migration velocity of each sample of suspension studied was determined by means of the U-tube. (It was found impracticable to employ the methods of the microscope or ultramicroscope cells for these determinations because of poor resolution or agitation caused by excessive gassing with most samples treated with acid.) Very sharp and stable boundaries were obtained from mixtures both treated and untreated with electrolyte. Comparison of these data should give an indication of the influence of the particle charge on flocculation and precipitation.

The coagulating agent used was sulfuric acid. Sufficient amounts of a solution (0.945 N) were pipetted into the different samples of suspension to give concentrations of 11.7, 23.0 and 66.0 milliequivalents of the acid per liter. Preliminary experiments in test-tubes indicated that a most efficient concentration might be found between these limits. Each addition was made over a period of five minutes, with vigorous mechanical stirring which was then continued for five minutes more. The suspensions were then immediately placed in the settling tube and observations begun. Thus, the "age" of each suspension was the same as every other.

During the additions of acid the appearance of all the mixtures was appreciably altered, usually to a more opaque, white color, and in some cases flocculation was apparent by the formation of comparatively large clumps visible to the eye.

A centimeter scale was etched on the front wall of the settling tube so that "h," the height of suspension, could be obtained by inspection, at any time during the run, and calculations could be made as readings were taken.

The formula derived for use with this tube[1] is:

$$\text{Fraction settled} = \alpha = \frac{d \tan b}{h(D - d_m)} (l_1 - l_2) \qquad (3)$$

where d is the density of the liquid in the side-arm, b is the angle described with the horizontal by the side-arm, h is the height of suspension, D and d_m are the densities of suspension and medium, respectively; l_1 is the side-arm meniscus level before settling has occurred, and l_2 is that at any time after-

ward. Typical data used and obtained with this equation are given in Table II for one sample of fraction-1. It is apparent by comparison of these data and the settling curve (Fig. 3) plotted from them that it has been necessary to use only representative points to describe the curves. The value of

TABLE II

Rate of Settling of Fraction-1
(Not flocculated)

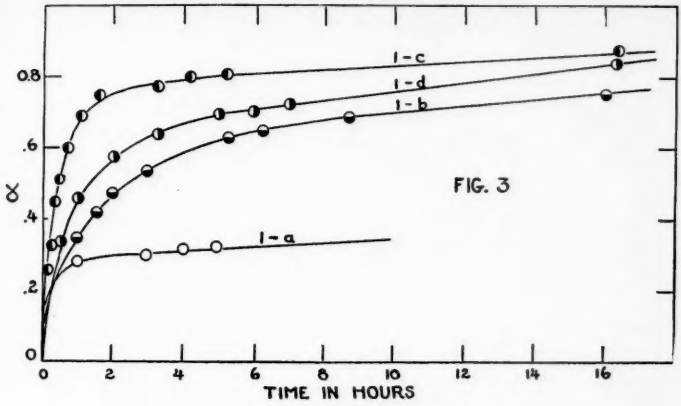
$D - d_m = 0.0065$
$h = 18.15$ cm.
$\tan b = 0.0175$
Fraction settled $= 0.148\Delta l$

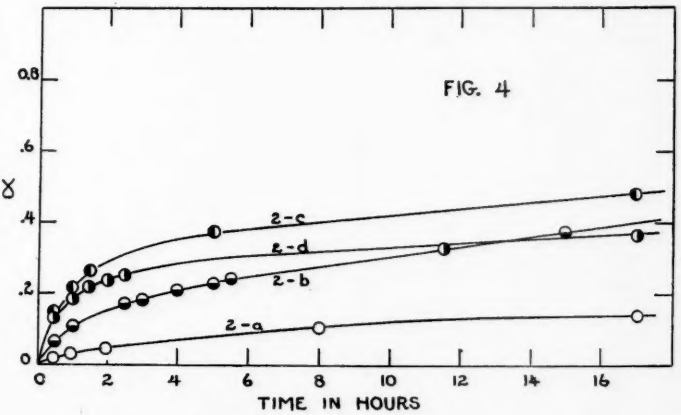
Time (Min.)	Reading	Δl	Fraction settled (α)
0	27.80 (ex.)	0	0
11	26.67	1.13	.168
12	26.60	1.20	.178
13	26.55	1.25	.185
14	26.49	1.31	.194
15	26.43	1.37	.202
17	26.37	1.43	.212
19	26.31	1.49	.221
23	26.18	1.62	.240
27	26.09	1.71	.253
32	26.04	1.76	.261
40	26.01	1.79	.265
53	25.97	1.83	.270
65	25.92	1.88	.278
75	25.88	1.92	.284
100	25.88	1.92	.284
(hours)			
3	25.80	2.00	.297
4	25.68	2.12	.314
5	25.62	2.18	.323
23	25.21	2.59	.383
44	24.80	3.00	.443

l_1 must be obtained by extrapolation back to zero time; hence, more readings were taken near the beginning of the run than later. Settling curves for all samples are given in Figs. 3, 4 and 5.

After the settling rate and migration velocity (Table III, Fig. 6) of a given coagulated suspension had been obtained, the medium was separated in a basket-type centrifuge at about 2000 R.P.M. Brief examination in an arc-light beam of all the media obtained showed no Tyndall cone in any case. Determinations of surface tension, density, viscosity, and acidity were made on this liquid. All measurements, except acidity, were made in the same thermostat at $25 \pm 0.1°$ C. Therefore, the results are strictly comparable as regards temperature.

Surface tension was determined by the method of maximum-bubble-pressure [12] with an accuracy of 0.3%. Densities were found with the usual





type of U-pyenometer, and an Ostwald viscometer gave values of viscosity (Fig. 7) with an accuracy of approximately 0.2%. These properties of the media studied are collected in Table IV.

The acidity of the medium in each instance was determined by titration with base standardized immediately before use. These data (Table V) make it possible to compare quantitatively the adsorbabilities of the different fractions. In Fig. 8, the broken line represents zero adsorption. Above this line, positive acid adsorption occurs (as with fraction-2), and below it, negative adsorption takes place (as with fraction-1 beyond a certain concentration of H_2SO_4).

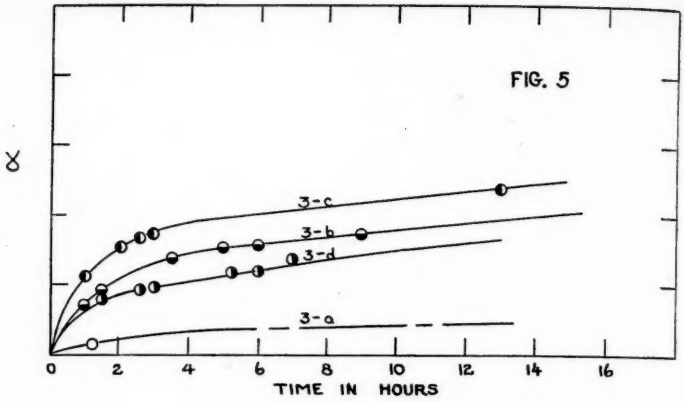


TABLE III

Migration Velocities of Suspensions

Sample No.	Equivalents H_2SO_4/L.	u (Microns/sec./volt/cm.)
(Whole sol)	None	2.7
1–a	None	2.65
1–b	0.0117	2.28
1–c	.0230	2.28
1–d	.0660	1.72
2–a	None	2.56
2–b	0.0117	2.36
2–c	.0230	2.19
2–d	.0660	1.30
3–a	None	2.94
3–b	0.0117	2.16
3–c	.0230	2.04
3–d	.0660	1.33
4–a	None	3.00
4–b	0.0117	(Electroendosmose)

Discussion

Since in all cases where acid has been added to these suspensions a clear liquid layer (showing no Tyndall effect) appears after a time at the top of the sample, and deepens slowly, it follows that all of the small particles indicated by the settling curves of the untreated suspensions have been assimilated into flocs by the acid. The "leveling off" of the settling curves for the flocculated samples must then largely be due to, and an indication of, the rate of compression of intermeshed flocs by their own weight, rather than a rate at which individual particles settle past each other. This behavior should be expected to be observed more closely with the finer fractions than with the first coarse fraction which contains an appreciable

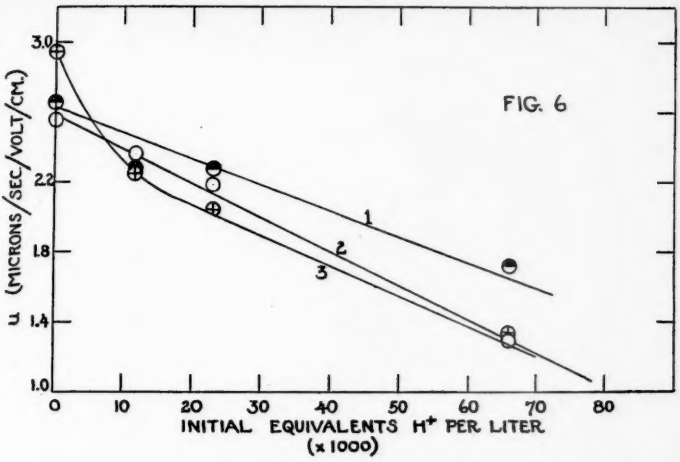


FIG. 6
u (MICRONS/SEC./VOLT/CM.)
3.0
2.2
1.8
1.4
1.0
0
10
20
30
40
50
60
70
80
1
2
3
INITIAL EQUIVALENTS H+ PER LITER
(x 1000)

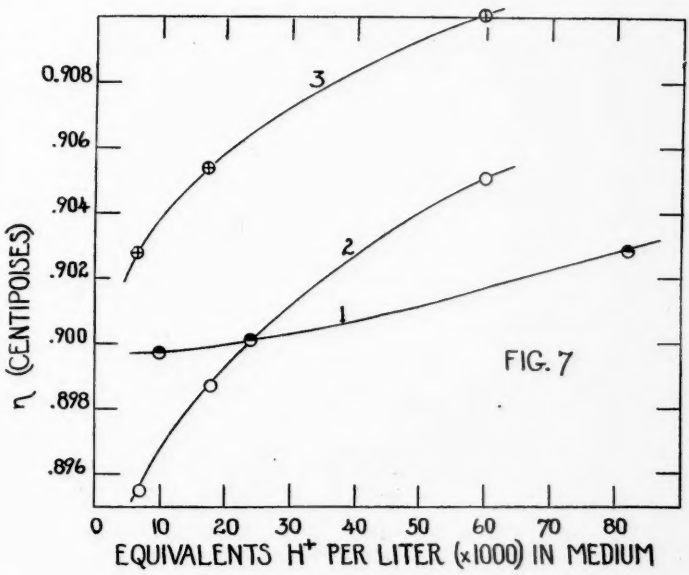


FIG. 7
η (CENTIPOISES)
0.908
.906
.904
.902
.900
.898
.896
0
10
20
30
40
50
60
70
80
1
2
3
EQUIVALENTS H+ PER LITER (x1000) IN MEDIUM

TABLE IV

Physical Properties of Media

Sample No.	Surface Tension (dynes/cm.)	Viscosity (Centipoises)	Density	Specific Conductivity ($ohms^{-1}$)
(1–a)	—	—	—	1.37×10^{-4}
1–b	71.96	0.8997	0.9977	2.71×10^{-3}
1–c	71.87	.9001	.9982	6.4×10^{-3}
1–d	71.52	.9029	.9997	1.32×10^{-2}
(2–a)	—	—	—	1.10×10^{-4}
2–b	71.86	.8955	.9977	2.60×10^{-3}
2–c	71.96	.8987	.9982	5.62×10^{-3}
2–d	71.87	.9051	.9997	1.38×10^{-2}
(3–a)	—	—	—	1.21×10^{-4}
3–b	—	.9018	.9976	2.6×10^{-3}
3–c	—	.9054	.9980	5.30×10^{-3}
3–d	—	.9101	.9996	1.36×10^{-2}
(4–a)	—	—	—	8.9×10^{-4}
(4–b)	—	—	—	2.65×10^{-3}

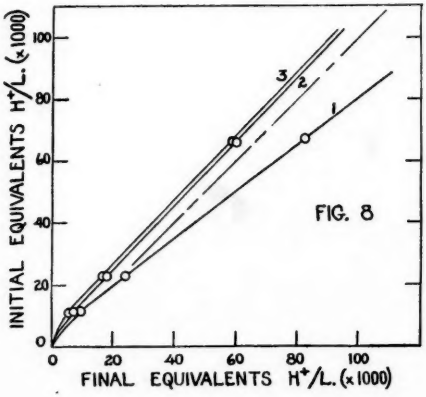


FIG. 8

percentage of comparatively large grains, leading to more compact floes of higher mean density. The interlacing of bentonite floes and the resultant "bridging" across the suspension's container was first suggested by Coward.[4]

Let a point P be considered, x centimeters below the surface of an infinitely deep column of a flocculated suspension of this type. If the weight of solid above the point P decreases with time, due to the compressive effect (extrusion of the medium) of its own weight, w, then at any time, t, in the

TABLE V

Adsorption

Sample No.	Equivalents H_2SO_4/L. Added (×1000)	Equivalents in Medium (×1000)	Adsorbed (×1000)
1–b	11.7	9.7	2.0
1–c	23.0	24.0	−1.0
1–d	67.5	82.0	−14.5
2–b	11.7	7.0	4.7
2–c	23.0	17.8	5.2
2–d	66.0	59.8	6.2
3–b	11.7	6.2	5.5
3–c	23.0	17.1	5.9
3–d	66.0	59.6	6.4

process:

$$-\frac{dw}{dt} = kw \tag{4}$$

and

$$\ln w = -kt + B \tag{5}$$

It is also true that

$$w = w_0(1 - \alpha) = k'(1 - \alpha) \tag{6}$$

where again α is the fraction settled at time t, and w_0 is the initial weight of solid above P. Combining (*5*) and (*6*), transferring to Briggsian logarithms, and collecting constants, there is obtained:

$$\log (1 - \alpha) = -Kt + C \tag{7}$$

When t is zero, α and log 1 are also zero, and (*7*) becomes:

$$\log (1 - \alpha) = -Kt \tag{8}$$

If the column is of finite depth, the situation is more complex. An increasingly greater resistance to settling is offered by the increasingly more dense and more viscous lower regions of the column. The latter factors are in turn determined by those inherent properties of the suspension (solid-liquid interfacial tension, thickness of the solvent "shell," mean particle density, charge, etc.) which control its degree of packing. For suspensions of lyophobic powders, Robinson [11] has very successfully assumed that packing will continue to the volume observed in the dry bulk. That the same assumption is not valid in the cases studied here is evident at once.

If it may be assumed that the time required for a given weight to settle past the point P is a parameter of the increasing resistance to the settling of that weight, and that other controlling factors do not vary for a given sample and may be collected into a single constant, then, if the resistance increases directly with time,

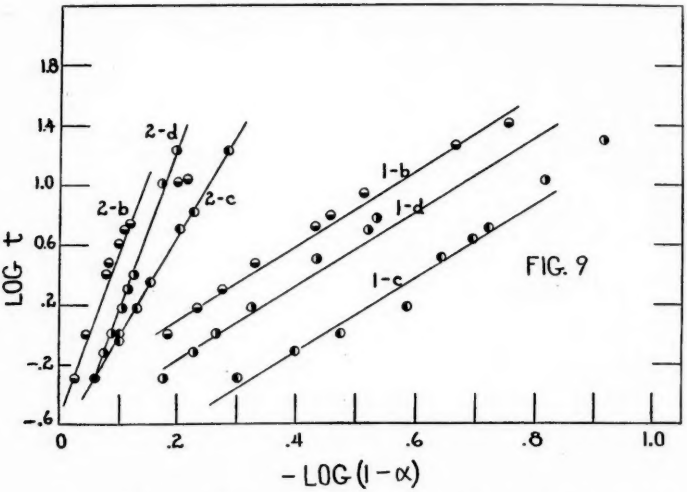
$$-\frac{dw}{dt} = k''\frac{w}{t} \tag{9}$$

and, simplifying after integration,

$$\log (1 - \alpha) = - A \log t + D \qquad (10)$$

where A and D are constants.*

In Figs. 9 and 10, equation (*10*) is tested with the data obtained with the first three fractions studied. The straight lines obtained for fractions-2 and -3 are good: the stray points for fraction-1 may be due to its settling behavior not meeting the conditions for which the equation was developed, as has been previously suggested.



The constant A (Table VI) should be dependent upon the particle charge (inversely), upon the difference in density of particle and medium (directly), upon the medium viscosity (inversely), and it is shown by inspection of the curves that the rate of settling and magnitude of A are dependent directly upon some function of the particle size distribution before coagulation. If, again, the latter and other factors influencing A be collected into a term E, and if the migration velocity may be considered a measure of particle charge, then:

$$A = E \frac{d_p - d_m}{u\eta_m} \qquad (11)$$

* Dr. Arthur E. Ruark, of the Physics Department of this University, has suggested by private communication the more general forms,

$$- \frac{dw}{dt} = k'' w \cdot f(t)$$

and

$$\log w = - A' \int f(t) dt + D'$$

where f(t) is a function of t, and in these expressions no assumption is made as to the specific relationship between t and the increasing resistance to settling.

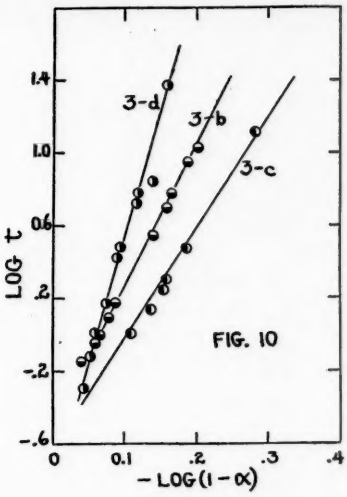


TABLE VI

A and E Values for the Various Suspensions

Sample No.	A	E
1–b	0.398	3.09×10
1–c	.403	3.12
1–d	.401	2.34
2–b	.090	0.72
2–c	.146	1.09
2–d	.090	0.40
3–b	.128	0.94
3–c	.166	1.15
3–d	.070	0.32

where E is a constant for each sample whose magnitude is determined by the particle size distribution and is characteristic of the nature of the suspension, u is the migration velocity, d_m and η_m are the medium density and viscosity, respectively, and d_p is the particle density. If d_p is assumed to be 2.75 in all cases, E may be evaluated (Table VI) for each sample from the data obtained in this study. The fact that the E values are not constant within each fraction may be interpreted as signifying a change in the inherent properties previously suggested in going from one sample to another, since the initial particle size distribution was the same in each case, within the same fraction. It would be of fundamental value to investigate these properties further.

These changes are further demonstrated by the viscosity and adsorption curves (Figs. 7 and 8). Referring to Fig. 7, curves II and III vary in

the general way to be expected from viscosity behavior on addition of sulfuric acid to water, in which the increase of viscosity in the more dilute region is quite rapid.* The form of Curve I can be explained by assuming (a) the presence in the solution of another component acting to depress the effect of the acid, or (b) the removal, by adsorption or otherwise, of more of the acid from the medium than is the case with fractions-2 and -3. The second possibility is obviated by the adsorption curve for fraction-1 (Fig. 8).

If the acid added were the only other component of the medium than water, all the points in Fig. 7 would fall on the same curve. Actually, it is observed that the dissolving or exchange effects increase with decreasing particle size. The conductivity of fraction-4 is nearly seven times greater than that of any of the first three fractions. This may be explained as a simple variation of solubility with particle size.

The surface tensions (Table IV) of the media do not vary beyond experimental error of the measurements. If they have any rôle in the settling process, it must be quite small. The surface tensions of pure sulfuric acid-water solutions at 25° change very slowly to about 20% acid by weight.†

The effect of initial particle size distribution on migration velocity is not appreciable before coagulation; on addition of the acid, the migration velocity is lowered more rapidly the smaller the mean particle size of the original untreated fraction (Fig. 6). This rate of lowering and the extent of adsorption of the acid vary together.

When the acid was added to fraction-4, the suspension became appreciably more viscous during stirring, and on standing without agitation, set to a gel. No measurable "compression settling" was observed with this gel for a period of three days. Centrifuging in the same basket-type centrifuge used to separate the media of the flocculated samples of the first three fractions failed to cause any separation with this sample, even under prolonged treatment. When placed in the U-tube for migration velocity determination, electroendosmose occurred instead of electrophoresis.

It is apparent that in the case of fraction-4, flocculation brings about such a degree of interlacing between flocs that very strong bonding results.

Hence, it may be concluded that the influence of initial particle size on the process of flocculation and precipitation of bentonite sols is one of determining the shape and structure of the floc formed. The results obtained here show that the smaller the mean particle size distribution in the unflocculated suspension, the more feathery and lacy will be the resultant floc when a given precipitating agent is added. If the concentration of the dispersed phase be sufficiently high, the interference of one floc with another may materially deter the removal of the solid phase by sedimentation, even to the extent of preventing it entirely. It might be predicted, according to this concept, that the effect of increasing concentration is one of bringing the individual flocs closer together, enhancing the possibility for intertwining and interference, and diminishing the rate of clarification—the observed behavior.

When the concentration is held constant, as was done in this study, the amount of interference will depend upon the shape of the floc, which in turn has been shown to be dependent upon the degree of dispersion of the suspension before flocculation.

* *I. C. T.*, Vol. 5, p. 12—by extrapolation.
† *I. C. T.*, Vol. 4, p. 464.

The results of Olin and Peterson [10] on the rate of settling of bentonite are here confirmed in general: varying the acid concentration sixfold has only slight effect. The differences are, however, measurable, and it has been found here that the rate of settling of a given fraction is not directly proportional to the amount of acid added, since in none of the first three fractions was the highest acid concentration the most efficient precipitator.

The action of the acid is a double one; first, it causes the formation and growth of flocs, and second, its concentration further determines the shape and form of the floc within a given particle-size fraction. The first factor tends to cause sedimentation; the second may tend to retard it. In varying the two factors simultaneously, a maximum point should be encountered. Inspection of the settling curves in Figs. 3, 4, and 5 shows that this concentration of maximum efficiency lies between 0.0117 N and 0.0230 N, and that the influence of acid concentration on floc shape is not nearly so great as that of initial degree of dispersion.

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The Variation of Raw Cotton Constituents with Physical Properties

By R. F. NICKERSON, T. D. FONTAINE, and C. B. LEAPE *

Abstract

On the basis of a limited number of samples there appear to be correlations between the relative surface areas of cottons and wax and pectate contents, between fineness and nitrogen content and, possibly also, between fineness and alkalinity of ash. A large number of analyses on different cottons will be required to show the exact relationships.

THE choice of raw cottons for specific uses is an art rather than an exact science. The available physical methods of characterization require special apparatus and are time-consuming; consequently, they do not lend themselves to the bale-by-bale testing of large quantities of raw cotton. Suitable chemical methods have not yet been worked out but probably would have advantages in being more rapid, in utilizing relatively inexpensive equipment, and in minimizing sampling errors. Such methods cannot be established, however, until sufficient data on constituents and properties have been accumulated. This paper contains experimental findings which, while limited, may indicate some possible chemical approaches to the use-selection of cottons. Nitrogen, phosphorus, ash, alkalinity of ash, pectate, wax, weight-loss during kier-boiling, fineness, and bundle strength are reported for seven different cottons.

Materials and Methods

Seven different varieties of raw cotton † representing a considerable range in average fiber lengths and grown under similar soil conditions during the 1937 and 1938 crop seasons were used in the present experiments. The samples were carded ‡ and the clean card sliver was employed without further preparation.

The methods of determining wax, pectate, weight-loss during kier-boiling, and fineness have already been reported.[6] Total and organic-ammonia nitrogens were estimated on 3-gram samples by a semi-micro modification of the Kjeldahl-Gunning method.[1] Phosphorus was estimated colorimetrically in a solution containing the ash from 1 gram of raw cotton.[4] Ash and alkalinity of ash were determined by the methods of Fargher and Probert.[2] Bundle strengths were ascertained § by the improved Chandler

* Cotton Research Foundation Fellowship, Mellon Institute, Pittsburgh, Pa.

† These samples were obtained through the courtesy of Mr. H. C. McNamara, Superintendent, Delta Experiment Station, Stoneville, Miss.

‡ Through the courtesy of the Cotton Spinning Laboratory, Agricultural Marketing Service, U. S. Department of Agriculture, Clemson, S. C.

§ Through the courtesy of the Cotton Fiber Laboratory, Agricultural Marketing Service, U. S. Department of Agriculture, Washington, D. C.

method.[7] Spectrograms of cotton ash were obtained by volatilizing equal weights of the ash in a carbon arc. The plates were compared and read by inspection.

Data

The various data are presented in the following two tables. The physical properties, growth seasons, and varieties are given in Table I; the results of the chemical analyses calculated in terms of the dry weight of the raw cotton are presented in Table II.

Table I

Physical and Vital Data on Raw Cotton Samples

Variety	Crop Season	Staple Length [a]	"Fineness" [b] (cm./mg.)	Bundle Strength (Pounds/sq. in.)
Half & Half.....	1937	7/8 inch	441	68,100± 700
Rowden.....	1938	1 "	461	80,600± 900
Wilds-5.....	1937	1 3/32 "	565	82,300± 900
Acala.....	1938	1 "	610	81,700± 600
Express.....	1938	1 1/32 "	621	80,500± 800
Delfos.....	1938	1 1/32 "	826	73,900± 400
Sea Island.....	1938	1 1/4 "	847	96,000±1600

[a] Estimates supplied by Cook & Co., Memphis, Tenn.
[b] The reciprocal of the more usual fiber-weight-per-centimeter.

Table II

Chemical Constituents of Raw Cottons as Percentage of Dry Weight

Variety	Wax %	Pectate %	Organic-Ammonia Nitrogen %	Total Nitrogen %	Phosphorus %	Weight-loss during Kier-boil %	Ash %	Ash Alkalinity * cc. N/1 H_2SO_4
Half & Half.....	0.44	0.43	0.132	0.140	0.020	7.0	1.01	13.0
Rowden.....	0.60	0.58	0.127	0.129	0.020	7.1	1.14	14.2
Wilds-5.....	0.70	0.60	0.147	0.144	0.020	7.8	1.11	14.6
Acala.....	0.75	0.69	0.165	0.172	0.020	8.0	1.20	13.6
Express.....	0.90	0.77	0.168	0.168	0.019	8.2	1.17	14.8
Delfos.....	0.87	0.71	0.172	0.174	0.019	8.6	1.26	15.4
Sea Island.....	0.89	0.76	0.232	0.234	0.022	8.5	0.80	16.3

* Defined [2] as milli-equivalents of sulfuric acid to neutralize one gram of ash.

Spectrograms of the fiber ash of the coarsest variety, Half and Half, and of the finest variety, Sea Island, revealed the presence in varying amounts in each cotton of the following elements:

Phosphorus	Barium	Sodium
Copper	Strontium	Potassium
Magnesium	Aluminum	Manganese
Calcium	Silicon	Iron

Discussion

Inspection of the data in Table II brings out several points of interest. First, between wax and pectate, there is a linear relationship which has been discussed in a previous paper.[6] Secondly, because total nitrogen does not differ materially from organic-ammonia nitrogen, it appears that appreciable quantities of nitrates and nitrites are not present in raw cotton. The observation of Ivanova and Kurennova [5] that 25–35 per cent of the nitrogen is in the form of nitrates and nitrites is, therefore, not confirmed. Thirdly, phosphorus content is relatively constant in agreement with the statement of Geake [3] that the amount is largely determined by local conditions of growth. Fourthly, the ash content fluctuates widely but the ash alkalinity does not. The observed values agree fairly well with corresponding ash and ash alkalinity data of Fargher and Probert [2]; viz., for North American cotton, ash 1.17 per cent, ash alkalinity 14.1, and for Sea Island, ash 0.98 per cent, ash alkalinity 15.2. Lastly, when the two tables are compared, it can be seen that the ash alkalinity, wax, pectate, and nitrogen appear to increase with increasing fineness.

The relationships between wax and fineness and between pectate and fineness are probably curvilinear.[6] Both of the latter constituents occur on the outside surface of the fibers and may be proportional to relative surface areas.

The nitrogen-fineness relationship shown in Fig. 1 is possibly of sufficient interest to warrant further investigation. Since fineness is plotted

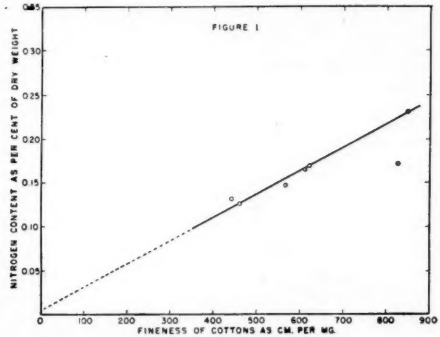

Fig. 1. The possible relationship between fineness and nitrogen content for various cottons is indicated.

as the number of centimeters of cotton which weigh one milligram, this relationship suggests that the nitrogen of raw cotton is distributed more or less uniformly along the length of the fibers. Evidence from microscopic examinations indicates that the likeliest source of this nitrogen is the protoplasmic residue in the fiber lumen. Inasmuch as fibers, during growth, attain approximately their mature lengths before secondary wall formation or internal thickening begins, it is conceivable that thin-walled or immature fibers could contain proportionally more nitrogen than fully-

matured or thicker-walled fibers of the same type. Ridge[8] has, in fact, observed that broken and immature fibers contain slightly more nitrogen than mature fibers of the same kind.

A single point on the nitrogen-fineness graph, representing Delfos, falls far below the line of the others. Thus, Delfos appears to contain *less* nitrogen than would be expected from its fineness. The other chemical constituents of Delfos do not seem to reflect this peculiarity. In bundle strength, however, this same sample appears to be far below the expectation for a cotton of its length and fineness. A reasonable explanation for this abnormality is not apparent from the available data.

This paper summarizes the work which has been done in this laboratory on the characterization of raw cottons by chemical methods. Attention is invited to this field because much experimental work is needed to establish the significance of the observations and to explore adequately some of the more promising leads. Information emanating from such studies may find valuable application in the choice of cottons for specific uses.

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Terms Relating to Hand of Fabrics

AT a joint meeting of representatives of the American Association of Textile Chemists and Colorists Research Committee's Sub-Committee on the Technical Evaluation of Textile Finishing Treatments and the corresponding committee of the Textile Committee D-13 of the American Society for Testing Materials held at the Chemists' Club in New York City on September 18th, 1940, the following tabulated proposed terms were suggested for designation of the physical properties of fabrics relating to "hand."

The words chosen represent the physical properties on one hand and the corresponding elements of "feel" on the other and were selected to be the least ambiguous or objectionable of the several that were considered. It was attempted to collect a series of terms which would be simple and understandable to the layman as well as to the engineer and scientist. They are not to be understood in a highly specialized sense, although certain of them have been used in such connection in other fields. It is suggested for consistency and better understanding among those dealing with the hand of fabrics that the proposed terms be used regularly in preference to the many other terms which might be substituted for them. Comments and suggestions on the proposed terms are solicited and may be sent to any of the organizations or persons named above.

Proposed Terms to Be Used in Naming the Physical Properties of Fabrics Related to Hand and for Describing the Corresponding Components of Hand

Physical Property	Explanatory Phrase	Terms to Be Used in Describing the Range of the Corresponding Component of Hand
1. Flexibility	Ease of bending	Pliable (high) to stiff (low)
2. Compressibility	Ease of squeezing	Soft (high) to hard (low)
3. Extensibility	Ease of stretching	Stretchy (high) to non-stretchy (low)
4. Resilience	Ease of recovery from deformation in which rate of recovery is without limits and thus includes elasticity (instantaneous recovery)	Springy (high) to limp (low). Resilience may be flexural, compressional, extensional, or torsional
5. Density	Weight per unit volume based upon A.S.T.M. standard measurement of thickness and fabric weight)	Compact (high) to open (low)
6. Surface contour	Divergence of the surface from planeness	Rough (high) to smooth (low)
7. Surface friction	Resistance to slipping offered by the surface	Harsh (high) to slippery (low)
8. Thermal character ...	Apparent difference in temperature of the fabric and the skin of the observer touching it	Cool (high) to warm (low)

Abstracts

Committee on Abstracts and Bibliography:
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I. Fibers (Synthetic and Natural) and Fiber Analysis

Macromolecular Compounds. Natural and Synthetic Fibres. H. Staudinger. *Mell. Textilber.*, 1939, V. 20, P. 631–35; abs. in *J. Soc. Dyers Col.*, July 1940, V. 56, P. 323.

A survey of investigations on the theory of fibre structure indicates that the important physical properties of natural fibres, e.g. their tenacity and swelling properties, are due, not only to their bio-structure, but also to the shape and size of the molecules which constitute the fibre. This theory is supported by the preparation of synthetic fibres from polyoxymethylenes and polyethylene oxides. Such fibres possess a crystalline structure resembling that of natural cellulosic fibres and resemble the latter also in fibrillar structure, swelling power and formation of cross-linkages, but they have no technical importance on account of their water-solubility and sensitivity to chemical reagents. The importance of macromolecular structure, however, is emphasized, and developments in the manufacture of other synthetic fibres culminating in the discovery of PC (chlorinated polyvinyl chloride) and nylon fibres are surveyed. The latter is a polyamide derived from adipic acid and hexamethylenediamine, and, although the cellulose molecules in staple fibre are rather longer than the thread molecules in nylon, the latter has a much higher tenacity and compares very favorably with natural silk. Its high tenacity is attributed to the uniform structure of the thread molecules and its X-ray diagram indicates that it is even more highly crystalline than the cotton fibre. Nylon is made by condensing adipic acid with hexamethylenediamine in cresol or xylenol at about 200° C.

until a sufficiently high viscosity and degree of polymerization are attained, and consists of a mixture of long and short chains and homologous polymers. Unlike cellulosic or PC fibres it is not spun from its solutions, but by a stretch spinning process at 270°–280° C., and it is this process which is responsible for its outstanding fibre structure. The example of nylon fibre indicates that natural fibres, like natural dyes, are not necessarily the best, and that synthetic fibres should become serious competitors. (C)

THE MICELLAR STRUCTURE OF CELLULOSE AND ITS DERIVATIVES. O. Kratky. *Angew. Chem.*, 1940, V. 53, P. 153–162; abs. in *J. Soc. Dyers Col.*, August 1940, V. 56, P. 370.

A survey of theories on the micellar structure of natural cellulosic fibres indicates that there is complete agreement between all investigators as regards the conception of lamellae and fibrillae, but no agreement has been reached as to whether these elements are in direct contact or surrounded by a skin of another substance, or whether the fibrillae form a uniform micellar system or consist of short particles held together by a substance other than cellulose. Consideration of the internal structure of the fibrillae, based on the lengths of the micelles as determined by X-ray and viscosimetric measurements, indicates that the thread molecule passes through several areas of crystalline and morphous structure, and that the ends are preferably not in the amorphous areas, but are distributed irregularly throughout. The extraordinary elasticity of the cotton fibre supports this theory. According to modern conceptions it is generally acknowledged that cellulose esters and ethers form molecular rather than micellar solutions since osmotic mol. wt. determinations show no alteration in the degree of aggregation. It is noteworthy that, in cuprammonium solutions of natural celluloses, the number of ultra-microscopic particles varies with the origin of the cellulose. The decrease in viscosity resulting from pretreatment of the fibres with, e.g. hydrochloric acid, is ascribed by some investigators to degradation of the cement substance. This complete contrast between these observations, based on an enormous amount of experimental evidence, needs further consideration if definite conclusions are to be obtained. Solution of cellulose in the form of individual micelles is also considered, but its validity is disputed because when cellulose is dissolved as xanthate only one-half of the hydroxyl groups have reacted, as evidenced by the fact that the xanthate on methoxylation and hydrolysis yields only one-half the amount of methylated cellobiose anticipated. It is suggested that the micelles are arranged in such a way as to render only one-half of the hydroxyl groups available for reaction. According to another theory, solution of cellulose occurs as fringed micelles and only the fringes are available for xanthation and similar reactions. Reprecipitation of cellulose from its solutions is discussed on the basis of these four solution theories, but no definite conclusions are reached. Determination of the density of unstretched cellulose threads or films indicates that they contain very little free internal space, and that the adjacent longitudinal micelles must be more or less parallel, and therefore the variety of arrangements revealed in every microscopic examination can only be due to the addition effect of small mutual variations. This conception is supported by the diffused darkening exhibited in the centre of the X-ray diagrams. The mechanism of the deformation of threads and filaments of cellulose hydrate and cellulose derivatives, which occurs on stretching, is discussed. There is evidence that crystalline and amorphous substances occur in almost equal proportions in the fibre. (C)

VINYL CHLORIDE AND ACETATE CO-POLYMERIDE RESINS: PROPERTIES. S. D. Douglas. *Ind. Eng. Chem.*, 1940, V. 32, P. 315–19; abs. in *J. T. I.*, July 1940, V. 31, P. A363.

A general account is given of the production of vinyl chloride and acetate co-polymeride thermoplastic resins and how their properties are affected by the ratio of the constituents and the method of manufacture. Reference is made to two types containing 88–90 per cent. of the chloride, one having M.W. 16,000–19,000 and being used for spinning into staple fibre, and the other, with M.W. 20,000–23,000 for continuous filament spinning. Special features of fabrics and fishing nets and lines made from these resins are mentioned. (C)

II. YARNS AND FABRICS

BANDAGE MULL: PREPARATION. W. Sandt. *Textilber.*, 1940, V. 21, P. 160–161; abs. in *J. T. I.*, July 1940, V. 31, P. A373.

The production of bandage mull is discussed and advice is given on the preparation of warps and the most suitable weaving arrangements. (C)

CREASE RESISTING PROCESSES FOR TEXTILES. A. D. J. Piesse. *Rayon Text. Mo.*, August 1940, V. 21, P. 58–9.

Presented at the American Association of Textile Technologists, June 5, 1940. (C)

THE CÜSTRIER PROCESS FOR INCREASING THE WEAR RESISTANCE OF TEXTILES. A. Hilbrig. *Monatschr. Textil-Ind.*, 1939, V. 54, P. 262–3; abs. in *C. A.*, 1940, V. 34, Col. 5288.

The wear resistance is increased by the incorporation of various amts. of fats. (C)

HYDROPHILE COTTON, BANDAGE, HOSPITAL AND SANITARY COTTON AND THEIR PRACTICAL, SIMPLE MANUFACTURE. H. Rehmann. *Monatschr. Textil-Ind.*, V. 55, P. 67–9 (1940); *Chem. Zentr.*, 1940, I, P. 3346; abs. in *C. A.*, 1940, V. 34, Col. 5287.

The treatments include boiling with NaOH solns., bleaching with $Ca(OCl)_2$, acidification, washing, soaping and acidifying with dil. H_2SO_4. (C)

IMPROVED ACTION SCOURING MACHINE. G. L. Atkinson. *Text. Col.*, Sept. 1940, V. 62, P. 601–603. (C)

LINSEED-OIL SIZE ON RAYON. Ciba Dyeing Laboratories. *Ciba Rev.*, 1940, V. 3, P. 1155–6; abs. in *C. A.*, 1940, V. 34, Col. 4919. (C)

MILLING SERVICE CLOTHS. *Wool Record*, 1940, V. 57, P. 762–63, 800–801; abs. in *J. T. I.*, July 1940, V. 31, P. A383.

The milling property of wool and the effect of milling on fabric strength are discussed. Practical details are given of milling procedure (with particular reference to the speed, time and temperature of the processing and to the care of the machines), and of the soap, grease and acid processes.

The results obtained by each of the three processes are considered in detail in relation to speed, and to the handle of the finished cloth. (C)

PHYSICAL AND CHEMICAL CHANGES PRODUCED IN BLEACHED COTTON DUCK BY CHAETOMIUM GLOBOSUM AND SPIROCHAETA CYTOPHAGA. Ruth E. Rogers, Helen G. Wheeler and Harry Humfeld. *U. S. Dept. Agr. Tech. Bull.*, 726, 35 pp. (1940); abs. in *C. A.*, 1940, V. 34, Col. 5287. (C)

PROPER EVALUATION OF SPECIAL FINISHES FOR TEXTILES. Ephraim Freedman. *Rayon Text. Mo.*, August 1940, V. 21, P. 55–57.

Presented at the American Association of Textile Technologists, June 5, 1940. (C)

SILK AND COTTON SEWING THREAD CONSTRUCTIONS. Henry Miedendorp, Jr. *Rayon Text. Mo.*, April 1940, V. 21, P. 78–9. (C)

SIZING OF RAYON YARNS. G. E. Wilson. *Text. Mercury and Argus*, Jubilee No., Sept. 1939, P. 159–161; abs. in *C. A.*, V. 34, Col. 4580 (1940).

Methods, app., and sizing products are reviewed. (C)

SIZING WARPS CONTAINING SPUN RAYON. Herbert C. Roberts. *Rayon Text. Mo.*, April 1940, V. 21, P. 73–4; May 1940, V. 21, P. 67–8.

The author holds that it can be safely stated that spun rayon warps and warps containing combinations of spun rayon, acetate, wool and other fibres can be sized for weaving with the existing equipment in most mills by the proper selection of materials on the market, and that the proper technique is within reach of all who will use ingenuity and common sense. (C)

SLIP-DRAFT SPINNING OF LONG VEGETABLE FIBRES. S. A. G. Caldwell. *Text. Mfr.*, July 1940, V. 66, P. 264–66, 268.

Explains recent developments in a comparatively new method of preparing and spinning smooth, long vegetable fibres for coarse yarns. (C)

SOME RECENT FIBRE-LATEX DEVELOPMENTS. M. C. Teague. *Am. Dye. Rptr.*, Aug. 19, 1940, V. 29, P. P422–P426. (C)

STAPLE FIBRE AND RAYON: EFFECT OF TEMPERATURE AND RATE OF LOADING ON STRENGTH. H. Lohmann. *Kunstseide u. Zellwolle*, 1940, V. 22, P. 64–66; abs. in *J. T. I.*, June 1940, V. 31, P. A332.

When acetate and viscose staple fibres were treated with water at different temperatures and the wet strengths determined by means of a Schopper fine-fibre tester which gives an approximately constant rate of extension, the losses in strength at higher temperatures, especially with acetate staple fibre, were much lower than those found by Breuer when using the Krais-Keyl Deforden strength tester in which the load is increased at a constant rate. Rayon yarns tested with the Baer Serimeter (approximately constant rate of extension) showed practically no decrease in wet strength at higher temperatures but a marked decrease in wet strength, especially in acetate yarns, was observed with the Richard Serigraph (constant rate of loading). The differences found with the different types of apparatus are due to the differences in the load-extension mechanisms. In practice, ex-

tension at a constant rate is of more importance than extension under a regularly increasing load and the restriction of staple fibre washing processes to temperatures below 40° C., as recommended by Breuer, seems unnecessary. (C)

A Study of the Influence, in Gilling, of Changes in Draft and Uncontrolled Distance, upon the Properties of English Processed Worsted Yarns and Fabrics made from Noble Combed Top. John C. Lowe. *Bull. of the Lowell Textile Institute*, August 1940. (C)

III. Chemical and Other Processing (Not Otherwise Classified)

Alizarin Red: Constitution. R. Haller. *Helv. Chim. Acta*, 1940, V. 23, P. 466–468; abs. in *J. T. I.*, July 1940, V. 31, P. A384.

In order to throw light on the chemistry of Alizarin red dyeing the author has sought to apply the supposed reactants in homogeneous solution. In one experiment, Al and Ca alizarates were dissolved with Turkey red oil in diethylene glycol. Cotton impregnated with this solution, dried and steamed for 2 hrs. at 0.5 Atm. was dyed bluish red, fast to soaping. In another test, Al and Ca ricinoleates and alizarin were dissolved in pyridine. This dyed cotton, after steaming, a somewhat bluish, intense pink, fast to soaping. (C)

Density of Wool in Relation to Acid Dyeing. P. M. Heertjes. *Atti X° congr. intern. chim.*, 1939, V. 4, P. 755–762 (through *C. A.*, 1940, V. 34, Col. 3094); abs. in *J. T. I.*, July 1940, V. 31, P. A386.

A study of the mechanism of the dyeing of wool by acid dyes. (C)

The Dyeing of Staple-Rayon Union Cloth. H. Brandenburger. *Deut. Wollen-Gewerbe*, V. 71, P. 1564–6 (1939); *Chem. Zentr.*, 1940, I, P. 1749; abs. in *C. A.*, V. 34, Col. 4576 (1940).

The fastness of the dyeing, strength of the textile, the sep. dyeing of staple rayon and wool, dyeing phenomena of wool in the acid and isoelec. region, proper conditions for fast dyeing, protection of staple rayon during dyeing, dyeing of flake wool and staple rayon, chem. fundamentals of the dyeing of wool, and the importance of the proper pH for max. protection of the fibre (optimum pH = 4.9) are discussed. Dyeing procedures are given covering the use of Cr dyes, AcOH, formic acid and NH_3. Prolonged exposure of the wool to the base has an unfavorable effect. The fibre is damaged by fungi; this can be prevented by the antiseptic action of K_2CrO_4. Cr dyeings are more advantageous than vat dyeings which are fast to light. Staple rayons must be treated very carefully to preserve wear resistance. S dyes are preferable to vat dyes, which must be used in the presence of stronger alkalies. (C)

Enzyme Desizing Efficiency. Quantitative Evaluation. Walter M. Scott. *Ind. Eng. Chem.*, 1940, V. 32, P. 784–7; abs. in *C. A.*, 1940, V. 34, Col. 4920.

Two newly developed lab. methods for studying the desizing efficiencies of com. malt enzymes, animal enzymes and bacterial enzymes are described. The immersion method corresponds to the treatment which cotton fibres

receive in jigs or overhead reel barks. The padding method is similar to the padding practice as is commonly used for desizing. Data indicating the relative efficiencies of the above enzymes and of both methods are presented. (C)

ENZYMES: USE IN THE TEXTILE INDUSTRY. L. Mayer. *Textilber.*, 1940, V. 21, P. 176–78; abs. in *J. T. I.*, July 1940, V. 31, P. A382.

Enzymes used in the textile industry are classified into (1) vegetable diastases (malt amylases), (2) animal amylases (pancreas amylases), (3) bacteria amylases (Biolase and Rapidase), and (4) mould diastases (Taka-diastase), and the nature, characteristics and textile applications of each group are discussed. (C)

GROUP-WISE DETECTION OF ORGANIC DYESTUFFS WITH FERROUS HYDROXIDE. Herman Eichler. *Z. anal. Chem.*, V. 119, P. 91–4 (1940); abs. in *C. A.*, 1940, V. 34, Col. 4912. (C)

HYPOSULFITES AND THEIR DERIVATIVES. STRUCTURE, DEVELOPMENT AND USE IN THE TEXTILE INDUSTRY. G. S. Ranshaw. *Chem. Age* (London), V. 41, P. 359–60 (1939); abs. in *C. A.*, V. 34, Col. 3924 (1940).

A review of the constitution and manuf. of $Na_2S_2O_4.2H_2O$ and of the constitution and uses of Na hyposulfite-CH_2O complexes. (C)

AN IMPROVED METHOD FOR DYEING WITH BASIC DYES WITH TANNIN MORDANTS. A. V. Boguslovskii. *Klopchato-Bumazhnaya Prom.*, 1939, No. 1, 51; *Khim. Referat. Zhur.*, 1939, No. 6, P. 101; abs. in *C. A.*, 1940, V. 34, Col. 3920 (1940).

Sb salts are introduced directly into the tannin print in the presence of $H_2C_2O_4$. More stable colors are obtained by this method owing to the absence of intermediate drying of the tanned substance. (C)

INDANTHRENE AND ALGOL RESERVES UNDER RAPIDOGEN COLORS. Hans Gürtler. *Mell. Textilber.*, V. 21, P. 126–7 (1940); abs. in *C. A.*, V. 34, Col. 4573 (1940).

Rapidogen Developer NN, an organic base which dissolves naphthols of the As series and is volatile with steam, makes possible the development of Rapidogen colors in a steam ager without the use of acid. Caustic alkali prevents development under these conditions, and underprints of vat colors can be reserved if the paste contains 5% free NaOH. Of the Rapidogens the reds and oranges give good overprints with all vat colors. The blues, violets and greens give good overprints with most of the vat colors but weaken the shades of the following: Indanthrenes Red Violet RRN, Brilliant Rose R, Brown RRD, Printing Blues GG, B, and R and the Brilliant Indigo series. Many new possibilities which this process offers to the textile printer are mentioned. (C)

INJURY BY ACID AND ALKALI TO FABRICS OF DEGUMMED SILK UNDER THE ACTION OF HEAT AND LIGHT. Michele Bonicatti. *Boll. ufficiale staz. sper. seta*, 1937, V. 7, P. 90–7; *Chem. Zentr.*, 1938, II, P. 1701; abs. in *C. A.*, 1940, V. 34, Col. 4919.

Silk was treated with dil. acids and dil. alkalies of increasing concn. (0.5–5%). Its phys. properties were then tested with the serimeter im-

mediately after such treatment, again after heating at 60° for 6 hrs., and after exposure to light for 65 days. From the great no. of data reported in tables and curves it is apparent that silk which is to be further processed and thus exposed to heat and light should not be treated with mineral acids. Treatment with HOAc is safe and has no effect on the dynamometric properties. Citric acid had a definitely corroding action. If the use of a mineral acid in dyeing cannot be avoided, then the silk should be subsequently treated with AcONa. The results of Harris indicating that treatment with alkalies has a protective effect against the action of light could not be substantiated. (C)

IV. Research Methods and Apparatus

Cotton-Staple Fibre-Cottonized Hemp Mixtures: Analysis. A. Cappelli and R. Tuffi. *Boll. Assoc. Italiana Chim. Tess. e Col.*, 1940, V. 16, P. 2–10; abs. in *J. T. I.*, July 1940, V. 31, P. A396. (C)

Determination of Lanital in Mixed Fabrics Containing Natural Wool. G. Chessa. *Chim. ind. agr. biol.*, 1940, V. 16, P. 37 (through *C. A.*, 1940, V. 34, Col. 3096); abs. in *J. T. I.*, July 1940, V. 31, P. A400.

Wash 1 g. of sample with alcohol, ether, and with water, dry at 110–20°, treat with 50 c.c. of a reagent formed from 100 c.c. of 28° Be glycerol and 15 c.c. of 10% hydrochloric acid, and boil under reflux condenser for exactly 3 min. Dilute the solution with 50% alcohol, filter, wash the insoluble matter, dry at 110–20° and weigh. The reagent dissolves lanital but not natural wool. (C)

Evaluation of Staple Fibre. Eisenhut. *Angew. Chem.*, 1939, V. 52, P. 568–572; abs. in *J. Soc. Dyers Col.*, July 1940, V. 56, P. 330.

The mechanical and chemical properties of staple fibres are so entirely different from those of cotton that quite different tests are necessary for their control during use. These include an accurate determination of extensibility, with particular reference to the elasticity and plastic behavior of staple fibre; determination of the degree of polymerization, with particular reference to the influence of the degree of polymerization on alterations to the fibre produced during use; examination of the splintering effect and its causes. The extent to which other physical properties, e.g. bending strain, rubbing and torsional strength, may be used in evaluating staple fibres is to be discussed later. (C)

Jute: Determination in Mixtures with Hemp. A. Cappelli and R. Tuffi. *Boll. Assoc. Italiana Chim. Tess. e Color.*, 1939, V. 15, P. 117–121; abs. in *J. T. I.*, July 1940, V. 31, P. A395.

A method for the determination of jute in fabrics woven from jute-hemp mixture yarns depends on extraction of the hemp by cuprammonium solution, the concentration of the solution and time of treatment being varied according to the composition of the fibre mixture determined approximately by microscopic observations. Details of the procedure and typical results are given. (C)

LANITAL: DETERMINATION IN MIXTURES WITH WOOL. *Boll. Assoc. Italiana Chim. Tess. e Col.*, 1940, V. 16, P. 11–18; abs. in *J. T. I.*, July 1940, V. 31, P. A396.

A method for the determination of the Lanital content of Lanital-wool mixtures depends on dissolving the wool by treating a sample with a solution containing 20% of barium hydroxide (cryst.) and 25% of potassium nitrate. Details of the procedure are given and experiments with various alkali and salt solutions carried out in the development of the method are discussed. Typical results are given. Lanital which has been subjected to energetic dyeing or finishing treatment suffers a loss of 3–5% in the treatment described and the weight of Lanital found should be corrected by multiplying by the factor 1.03–1.05. (C)

LANITAL: DETERMINATION IN MIXTURES WITH WOOL. E. Cerbaro. *Boll. Cotoniera*, 1940, V. 35, P. 22–24; abs. in *J. T. I.*, July 1940, V. 31, P. A397.

The method of Hartung depending on solution of the Lanital in a pepsin solution, and the methods of Cappelli and Tuffi, and Gandolfo and Maceraudi ("AIL" method) depending on solution of the wool in sodium sulphide-caustic soda and barium hydroxide-potassium nitrate solutions, respectively, are briefly described and the results of tests of these methods are reported. The author has found difficulties in the final washing and considerable losses in weight of the Lanital when the method of Cappelli and Tuffi is applied to mixtures dyed with certain dyes. The pepsin method gives good results except in the case of Lanital which has been treated with a chrome mordant, such material being insoluble in the reagent. The method is long and laborious. The AIL method is sufficiently simple and rapid, is the most generally applicable, and gives the best results with both raw and dyed or chrome mordanted Lanital. (C)

A NEW PRACTICAL METHOD FOR DETERMINING OXYCELLULOSE IN BLEACHING PRACTICE. I. Ionescu-Muscel. *Mell. Textilber.*, 1940, V. 21, P. 119–121; abs. in *J. Soc. Dyers Col.*, July 1940, V. 56, P. 330.

Procedure is described for the rapid determination of oxycellulose and control of the degree of oxidation of cellulosic materials in the bleaching process. For this purpose, 2 g. of oxycellulose material to be examined and 250 c.c. water are introduced into a flask similar to that used in the Schwalbe method. As soon as the mixture reaches the boil, 100 c.c. Fehling's solution (see below) are added in small portions, and boiling continued for 15 min. Part of the copper is precipitated as copper oxide, and the excess of Fehling's solution is determined by titration with a standardized sugar solution (see below) at the boil, the burette being arranged over the flask standing in a boiling water-bath. For ease of determining the end-point it is advisable to stand the flask on a white base and traces of copper in the decolorized liquid are detected by filtering a portion through a double filter paper, acidifying with a few drops of acetic acid, and adding potassium ferrocyanide. If traces of copper are present, the liquid becomes black and titration is continued until this reaction can no longer be produced. The loss of liquid involved causes a negligible error if the spot tests for copper are not carried out until titration is as complete as possible. Determination of oxycellulose by this procedure requires 1½ hr. compared with 27 hr.

required by the Schwalbe method, and much higher copper numbers are obtained. Traces of hydrocellulose probably take part in the reaction, but they do not influence its practical value because they are not capable of diminishing the oxycellulose quantitatively. The sugar solution is prepared by introducing 9.5 g. pure, dry, refined sugar into a 1 l. graduated flask, adding 5 c.c. hydrochloric acid, sp. gr. 1.19, warming on the water-bath to 70° C. and then cooling to 20° C. A further quantity of hydrochloric acid is added, the solution neutralized with sodium carbonate and made up to 1 l. with water; 1 c.c. contains 0.005 g. invert sugar. For the preparation of the Fehling's solution—(a) 34.64 g. copper sulphate are dissolved in 500 c.c. water in a graduated flask. (b) A solution is prepared by dissolving 17.3 g. caustic soda in about 400 c.c. distilled water, cooling and making up to 500 c.c. This solution is kept in a flask closed with a cork. A second solution is prepared by dissolving 173 g. sodium potassium tartrate and 50 g. stick caustic soda in 400 c.c. distilled water, cooling, and making up to 500 c.c. These two solutions are mixed in equal proportions. Equal parts of solutions (a) and (b) are mixed just before use. The copper in 1 c.c of the resulting solution is precipitated by 1 c.c. of the sugar solution. (C)

V. Pure Science, Economics and Misc.

Intramolecular Folding of Polypeptide Chains in Relation to Protein Structure. H. Neurath. *J. Phys. Chem.*, March 1940, P. 296–305; abs. in *Eastman Kodak Abs. Bull.*, July 1940, P. 385.

The space requirements and orientation of amino-acid residues in fully extended and folded polypeptide chains have been investigated, using scaled atomic models. Accommodation of the side chains, formed by the amino-acid residues, may be readily brought about in fully extended polypeptide chains, chiefly owing to the fact that the side chains protrude alternately from the upper and lower surfaces of the plane formed by the main chain. This structure can account, almost quantitatively, for the observed film areas and properties of protein monolayers. Folding of polypeptide chains, in the manner suggested for alpha-keratin and supercontracted keratin, respectively, results in drastic changes in the orientation of the side chains. The data indicate that, unless unreasonable distortions of bond angles are assumed, these configurations are too condensed to permit residues, other than those of glycine and alanine, and hydrogen atoms to move into the positions called for by the carbon atoms of the hexagonal rings to which they are attached. From considerations of space requirements of amino-acid residues, it follows also that the cyclol structure is too condensed to permit the accommodation of side chains. The significance of these considerations for the problem of protein structure is discussed. (S)

Metal Stains. *Wool Record*, 1940, V. 57, P. 682–3, 686; abs. in *J. T. I.*, June 1940, V. 31, P. A334.

Details are given of the metals most widely used in textile processing and of the types of stains liable to occur. Methods are described in detail for the detection of copper, iron and chromium stains in wool. Methods for the removal of copper and iron stains are given. (C)

NOTES ON LOW-POWER PHOTOMICROGRAPHY. F. M. Duncan. *J. Photomicrographic Soc., (London)*, 1930–36, V. 16, P. 57–62; abs. in *Eastman Kodak Abs. Bull.*, April 1940, P. 179.

The article is chiefly a general discussion of the author's apparatus and technique. (S)

PASTING AND IDENTIFICATION OF STARCHES. Willard L. Morgan. *Ind. Eng. Chem.*, June 1940, V. 12, P. 313–17.

When starches are heated with water, the cloudy suspensions gradually become translucent as pasting occurs. A photo-electric method is used to follow this change at various temperatures, and characteristic curves for each type of starch are secured. Besides indicating the nature of the starch, the curves show progress and completion of pasting. Modified starches show progressive alterations in the curves. By simple mathematical relations the curves may be applied to analysis of mixtures of starches. (C)

PROTEINS IN THE TEXTILE INDUSTRY. J. Lotichius. *Chem. Weekblad*, 1939, V. 36, P. 407–13; abs. in *J. T. I.*, Feb. 1940, P. A118.

A table is given showing the chief physical and chemical properties of cotton, viscose, wool and silk. Nägeli's micellar theory and Katz's explanation of the swelling of fibrous substances are applied to these four fibres. A brief survey is given of their chemical properties, especially behavior with respect to water, and influence of acid and alkali in bleaching and dyeing. Fibre structure presupposes structural elements of high molecular weight which are able by polymerization to form long chain molecules. The specific character of protein fibres is due to their low heat conductivity and to their chemical properties as proteins. (C)

RAMIE CELLULOSE: REFRACTIVE INDEX; EFFECT OF TEMPERATURE. A. Frey-Wyssling and K. Wuhrmann. *Helv. Chim. Acta*, 1939, V. 22, P. 981–8; abs. in *J. T. I.*, Jan. 1940, P. A47. (C)

RESEARCH ON COTTON IS PLANNED AT NEW LABORATORY IN NEW ORLEANS. *Cotton*, March 1940, V. 104, P. 44–5. (C)

SEMIMICROESTIMATION OF AMINO ACIDS. H. R. Ing and M. Bergmann. *J. Biol. Chem.*, August 1939, V. 129, P. 603–7; abs. in *Eastman Kodak Abs. Bull.*, April 1940, P. 216.

A semimicrotechnique based on Bergmann's solubility method of analysis of protein hydrolyzate for amino acids is described. Data are given showing the use of the method for determining glycine, alanine, leucine, arginine, and proline. (S)

STRUCTURE AND PROPERTIES OF SYNTHETIC RESINS. H. V. Potter. *Text. Mfr.*, July 1940, V. 66, P. 276.

Abstract of part of a paper, "Plastics as Constructional and Engineering Materials," to the Royal Society of Arts (*J. R. S. A.*, No. 4563, P. 672). The bases of the different properties of the numerous new resin-like materials which have applications as raw materials, constructional materials, and some new artificial fibres. (C)